APPLICABILITY OF FUOSS EQUATION TO ELECTROLYTIC SOLUTIONS IN NON-AQUEOUS SYSTEMS

ABSTRACT

THESIS SUBMITTED FOR THE DEGREE OF

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IN

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BY

QUDSIA REHANA

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

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ABSTRACT

Electrical conductivity of dilute electrolytic solutions of tetra-alkyl (alkyl = Methyl, Ethyl, Propyl and Butyl) ammonium bromides in dioxane-water ($10.71 \leq D \leq 69.69$) and Ethylene glycol-water ($37.7 \leq D \leq 75.60$) mixtures has been measured as a function of concentration at 25° C. The density and viscosity of solvent mixtures have also been measured.

The concentration dependence of conductivity data for all salts under study has been analysed by Fuoss-1978, Justice, Pitts and Fuoss-Onsager-Skinner (FOS) conductance equations. The values of the limiting equivalent conductance, Λ_0, the Gurney cosphere diameter, R or the ion-size parameter, a°, the ionic-association constant, K_A and those of solvent separated ion-pair formation constant, K_R and the contact ion-pair formation constant, K_S are computed. The significance of these parameters has been emphasized in explaining the concentration dependence of conductance in terms of the dielectric constant and the viscosity of the medium. Such an analysis is investigating the ion-ion, ion-solvent and solvent-solvent interactions as well as the extent of ionic-association of tetra-alkyl-ammonium halides in the solvent mixtures under study. The overall values of the cosphere diameter and the ionic-association constant are

found to increase with a decrease in the dielectric constant of the solvent-mixtures.

Densities and viscosities of EG+H_2O mixtures containing 10, 20, 30, 40, 50 and 60 % by weight of ethylene glycol (EG) and those of their solutions with tetra-alkyl-ammonium bromide have been measured as function of temperature and concentration. The concentration dependence of viscosities and apparent molar volume, φ_v, of the electrolytic solutions has been explained in terms of the Jones-Dole and the Mason's equations, respectively.

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DEDICATED TO MY PARENTS

CERTIFICATE

This is to certify that the work presented in this thesis entitled, "APPLICABILITY OF FUOSS-EQUATION TO ELECTROLYTIC SOLUTIONS IN NON-AQUOUS SYSTEMS", is original, carried out by Mrs. Qudsia Rehana under my supervision and is suitable for the award of Ph.D. degree in Chemistry of this university.

(Prof. Saiduzzafar Qureshi)
Chairman, Dept. of Chemistry
A.M.U. Aligarh

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Qudsia Rehana

(Mrs. Qudsia Rehana)

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PART – A

INTRODUCTION

Studies on the transport properties of electrolytes in different solvents are of great importance to obtain informations on the behaviour of ions in solution[1-10]. Electrical conductance, being one of the important properties of electrolytic solutions which can be successfully explain the nature of the electrolyte and its interactions with various solvents, has been extensively studied during the last several decades and, therefore, the conductance theory has undergone a drastic change in the able hands of many workers[11-23], who interpreted their conductance data in the light of solute-solvent interactions. A survey of literature on electrolytic solutions reveals that it was as early as 1923 when the effect of ionic atmosphere on ionic mobility was first considered by Debye and Huckel[24]. Their theory proposed a linear relationship between the equivalent conductance and the square root of molar concentration. The theory was based on two main factors: (i) when an ion moves through a solution under the influence of an applied field, it tends to disturb the surrounding ionic atmosphere, which then exerts an opposing electric force, (ii) the ions comprising the ionic atmosphere produce a counter current of solvent which also retard the motion of the central ion.

However, Onsager[25-27] has pointed out that in calculating the relaxation effect, Debye and Huckle neglected the influence of the Brownian movement of ions and also employed a treatment that is valid only if the negative and the positive ions have equal mobilities.

Furthermore, he has shown that the electrophoretic effect could be calculated in a manner that does not involve the ionic radii. The important feature of Onsager's equation was the proportionality factors that could be readily calculated.

Onsager equation gave results which were found to be in close agreement with those obtained from the measured value at very low concentrations but such an equation was strictly valid only as a limiting expression. This was so because in the derivation of the simple equation only the first approximations were retained in the mathematical treatment and also the sample's physical picture assumed in the derivation might be inadequate for finite concentrations. The equation was

$$\Lambda = \Lambda_0 - \left[\frac{5.78 \times 10^5}{(DT)^{3/2}}\Lambda_0 + \frac{58.0}{(DT)^{1/2}\eta}\right]\sqrt{C} \qquad (1)$$

where the terms Λ_0, D, T, η and C refer respectively to the equivalent conductance at zero concentration, the dielectric constant of the solvent, absolute temperature, the viscosity and the equivalent concentration.

The above equation can conveniently be written as

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{C} \qquad (2)$$

This equation shows that the Λ bears a linear relationship with the square root of concentration C. The constants α and β are known as the relaxation and the electrophoretic effects, respectively, and they depend upon the nature of the solvent. Onsager's treatment confirmed the square root relationship between the Λ decrease and the concentration increase in the cases of extremely dilute solutions. However, in examining the conductivity it has been found that the values of Λ_0 calculated from eqn. (2) are not constant over the appreciable concentration range. Thus, Shedlovsky[28] suggested the following conductance equation,

$$\Lambda_0' = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} \qquad (3)$$

$$= \Lambda_0 + BC$$

or $$\Lambda = \Lambda_0 - S_\Lambda\sqrt{C} + \left(1 - \alpha\sqrt{C}\right)BC \qquad (4)$$

in which B is an empirical constant characteristic of each electrolyte having the same order of magnitude as that of S_Λ and has no theoretical significance. It is an interesting fact that for many electrolytes the slope B has almost the same values which are close to that of Onsager slope, $S_\Lambda = (\alpha\Lambda_0 + \beta)$. This equation was found to be applicable[36] up to 0.1 N concentration in the case of 1 : 1 electrolyte within the limits of experimental error.

Fuoss and Onsager[29] have explained the deviation of Λ versus √C plots from linearity by adding two terms to eqn. (2), which takes on the form,

$$\Lambda = \Lambda_0 - S_\Lambda \sqrt{C} + EC \log C + BC \qquad (5)$$

Equation (3) failed to explain the electrolytic conductance[30-36] of many electrolytes. Then, Fuoss and Hsia[30] developed a theory to minimize the discrepancies between Fuoss-Onsager theory[31, 32] and that of the Pitts[33] and proposed an equation of the form,

$$\Lambda = \Lambda_0 - S_\Lambda \sqrt{C} + EC \ln C + J_1 C - J_2 C^{3/2} \qquad (6)$$

where S_Λ is the coefficient of limiting law, E depends only on the properties of solvent and the charge of ions while J_1 and J_2 depend on the same parameters as well as on the distance 'a' of the closest approach of ions.

Fuoss and Kraus[35] used satisfactorily eqn. (6) with higher terms for the determination of association constants of quarternary ammonium salts and alkali halides in water and dioxane-water mixture at 25° C. The size of large ions, for example, quarternary ammonium ions, picrates and chlorates etc. which are comparable with those of

the solvent molecules were thought to be responsible for the ionic association.

Fuoss[36] modified eqn. (6) by taking into account such an association. To consider the effects of viscosity of the solution on equivalent conductance, Fouss considered Falkenhagen and Dole equations[37, 38],

$$\eta/\eta_0 = 1 + S\eta\sqrt{C} \qquad (7)$$

where

$$S_\eta = (\beta/320)\left(\frac{\Lambda_0}{\lambda_+^0\lambda_-^0}\right)\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\Lambda_0}\right)\right] \qquad (8)$$

A term known as Falkenhagen-Dole coefficient was defined as

$$F = [(\eta - \eta_0)/\eta_0]/\sqrt{C} \qquad (9)$$

where

$$F = \frac{\pi NR^3}{300} \qquad (10)$$

Thus, by accounting for such a viscosity effect, the conductance equation (6) assumes the form,

$$\Lambda = \Lambda_0 - S_\Lambda\sqrt{C} + EC\log C + JC - F\Lambda_0 C \qquad (11)$$

where

$$J = \left[\left(1 - \alpha\sqrt{C}\right)(1 - J_2/J_1)\sqrt{C}\right]J_1$$

Equation (11) has been found to be applicable in a variety of solvents to non-associated electrolytes only.

Fuoss[39, 40] further modified the said equation in which he considered that the neutral molecules of such electrolytes (having large ions) partially dissociate into free ions in solutions. He has applied the law of mass action to the association equilibrium,

$$A^+ + B^+ \rightleftharpoons A^+B^-$$

$$K_A = \frac{[A^+B^-]}{[A^+][B^-]} \qquad (12)$$

where K_A refers to association constant.

If f refers to the activity coefficient of free ions and γ denotes the fraction of the solute as free ions, equation (12) may be expressed as,

$$K_A = 1 - \gamma / C\gamma^2 f^2 \qquad (13a)$$

or $$\gamma = 1 - K_A C \gamma^2 f^2 \qquad (13b)$$

and $$-\ln f = \beta' C^{1/2} \gamma^{1/2} / (1 - \kappa_a \gamma^{1/2})$$

where $\beta' = 0.4343\ (e^2 / 2DKT)\ (8\pi Ne^2 / 1000\ DKT)$

The degree of dissociation, γ is defined as

$$\gamma = \frac{\Lambda}{\Lambda_i} = \frac{C_i}{C} \qquad (14)$$

Substituting the values of γ from eqn. (14) into eqn (13b), we get

$$\Lambda = \Lambda_i - K_\Lambda C\gamma f^2\Lambda \qquad (15)$$

where Λ_i is the equivalent conductance due to free ions at concentration C_i . The value for Λ_i may be obtained from eqn. (11) as,

$$\Lambda_i = \Lambda_0 - S_\Lambda\sqrt{C} + EC_i \log C_i + (J - F\Lambda_0)C_i \qquad (16)$$

Substitution of the value of Λ_i from eqn. (16) into eqn. (15) gives an expression for Λ which accounts for the association of the free ions also. The resultant equation is of the form,

$$\Lambda = \Lambda_0 - S_\Lambda\sqrt{C} + EC\gamma \log C\gamma + (J - F\Lambda_0)C - K_\Lambda C\gamma f^2\Lambda \qquad (17)$$

Thus, γ was calculated as

$$\gamma = \frac{\Lambda_{(obs)}}{\Lambda_0 - S_\Lambda\sqrt{C}\ \gamma_0 + EC\gamma_0 \log C\gamma_0 + JC\gamma_0} \qquad (18)$$

The resulting conductance equation as given by Fuoss[40] is

$$\Lambda = \gamma[\Lambda_0 - S_\Lambda\sqrt{C\gamma} + EC\gamma \log C\gamma (J - F\Lambda_0)C\gamma] \qquad (19)$$

where $S_\Lambda = \alpha\ \Lambda_0 + \beta$

$E = E_1\ \Lambda_0 - E_2$

$E_1 = 2.3026\ (\kappa^2\ a^2\ b^2 / 24\ C)$

$$E_2 = 2.3026 (\kappa a b \beta / 16 C^{1/2})$$

$$J = \sigma_1 \Lambda_0 + \sigma_2$$

$$\sigma_1 = (\kappa^2 a^2 b^2 / 12 C) [(2 b^2 + 2 b - 1)/ b^3 + 0.9074 + \ln (\kappa a / \sqrt{C})],$$

and

$$\sigma_2 = \alpha\beta + (11\kappa\beta a / 12\sqrt{C}) - (a b / 8\sqrt{C}) [1.017 + \ln ((\kappa a / \sqrt{C})]$$

Equation (19) has been satisfactorily employed[35, 36] in explaining the conductance behavior of associated electrolytes with variation in concentration.

The Fuoss-Onsager treatment conductance data through eqn. (19), which approximates to exclude the higher concentration terms $J_2C^{3/2}$ in comparatively two concentration regions shows that the values[41] obtained for the ion size parameters a° are low (2 – 10 A°). In certain cases[40] this equation gave negative values for the ionic association, which is physically unacceptable because the viscosity term, F has insignificant effect on the conductance in dilute electrolytic solution and therefore, neglected.

Justice[42-44] has, however, modified the said conductance equation by considering the higher order terms of concentration and the long-range interionic interactions. The modified equation is of the form

$$\Lambda = [\Lambda_0 - S_\Lambda \sqrt{C\gamma} + EC\gamma \log C\gamma + J C\gamma + J_{3/2}(C\gamma)^{3/2}] \qquad (20)$$

Eqn (20) is based on the Bjerrum interionic attraction theory and has been found to be good in the case of long-range interactions, while the Fuoss-Onsager eqn. (19) based on the Debye interionic attraction theory is capable of dealing with only short-range interactions. Fuoss-Onsager equation has been widely employed[11-21] particularly in the case of symmetrical electrolytes, while Fuoss-Justice equation[44] can satisfactorily explain the behavior of unsymmetrical electrolytes but its limited applicability cannot be overlooked. One can easily realize that both the equations cited above are complicated and involve too many approximations.

In 1975 Fuoss has proposed his primitive model[22] for the solutions of symmetrical electrolytes and computed the relaxation field and the electrophoretic counter current for the model using the continuum theory and thus a three parameter conductance function, $\Lambda(C; \Lambda_0, K_A, R)$ was obtained where Λ_0, K_A and R stood respectively for limiting conductance, association constant and the diameter of Gurney cosphere. This model of Fuoss represented the solution as containing the Gurney cosphere centered on ions of charge $\pm e$, When two oppositely charged cospheres overlap, the corresponding ions are counted as non-conducting pairs and are deleted from the population of ionic atmosphere.

and surrounded by the continuum containing a continuous space charge that integrates to $\pm e$.

The well-known hard sphere[32-45] model has two features in common: (i) use of the same model (rigid, charge spheres in a continuum), and (ii) calculation of the theoretical behavior of the model. But the operation of this equation involves the counting of some short-range interactions twice. This equation has been employed to explain the conductance-concentration behavior of symmetrical electrolytes. It has been found that for electrolytes whose ionic volumes are large compared to the volume of the solvent molecules, a good correlation is found between the distance parameter, R and the center-to-center distance of the ions, a'. Furthermore, the values of a' calculated by Stoke's hydrodynamics from Λ_0 and those calculated by the Boltzman statistic and the classical electrolytic theory from K_A agree with the value of R. In such a case the conductance function reduces to one parameter equation, $\Lambda = \Lambda(C; a)$. But in cases where ionic and solvent volumes are comparable, usually $a_\kappa \neq a_K \neq a_\Lambda$, all the three vary in an erratic way for a given electrolyte in different solvents or with composition for solutions in mixed solvents[46, 47]. The reason for the deviation is obvious, real ion in real solvents are not rigid charged spheres in continuum. While the theory based on the primitive model[34-42] gives a good account of the long-range* interactions (ion-ion and ion-solvent), which can only be described by the parameters characteristic of systems.

ionic interactions, it ignores all the detailed short range

Because of the discrepancies between the theoretically derived values of the parameters and the parameters characteristic of the real physical system, Fuoss[48] has reviewed all the previous theories for the electrolytic conductance.

Thus, Fuoss[48] proposed the theory of steady-state diffusion model. In previous theory for non-conducting pair $p = \gamma$ while in diffusion theory $p \neq \gamma$. He has considered an anion at a distance $r = R$ from a cation, which may either diffuse further away, or it may diffuse towards the cation (interchange positions with solvent molecules inside the cosphere) and eventually form a contact pair $A^+ B^-$. Along its diffusion path, it is thermal motion subjected to the force exerted by the external field and some of the diffusion-paired ions contribute to the transport current ($p > \gamma$). He further considered the behavior of contact pair, when the field is applied, the pair will tend to orient itself in the field; if the field is turned off after a time lag the pair will return to random orientation by diffusion without changing center-to-center distance, γ; $a \leq \gamma \leq R$ in which a is the constant distance and R is the diameter of the Gurney cosphere. In other words, contact pairs behave like diploes and contribute only to charging current but not to net transport of charge. A fraction α of these parts diffuse to contact to form non-conducting dipolar pairs,

$$\alpha/(1-\alpha) = \exp(-E_s/KT) \qquad (21)$$

in which E_S is the difference in energy between the diffusion pairs when ions in state γ = R and state γ = a. This model permits the separate treatments of short-range as well as of long-range interionic effects. The former (relaxation and electrophoretic) effects depend upon the value of R, the dielectric constant and the viscosity of pure solvents. The latter (formation of dipolar pairs) is described by the E_S or alternatively by $K_S = \exp(-E_S/KT)$ in which K_S is a constant describing the steady-state between the solvent separated diffusion pairs and the dipolar (contact) pairs.

Thus, beginning with the symbolic equation,

$$\Lambda_{(c)} = P\,[\Lambda_0(1+\Delta X/X) + \Delta\Lambda_e] \qquad (22)$$

where P is the fraction of the solute that contributes to the transport current, Λ_0 is the limiting value $\Lambda(0)$, $\Delta X/X(\leq 0)$ is the ratio of relaxation field to that of external field and $\Delta\Lambda_e(\leq 0)$ is proportional to the electrophoretic counter current for symmetrical electrolytes. Fuoss finally obtained the conductance equation[49, 50] as,

$$\Lambda = [1-\alpha(1-\gamma)]\,[\Lambda_0(1+\Delta X/X) + \Delta\Lambda_e] \qquad (23)$$

Analysis of conductance data by use of parametric eqn. (23) [$\Lambda = \Lambda(C; \Lambda_0, \alpha, R)$ or $\Lambda(C; \Lambda_0, K_A, R)$] requires relationship between α, γ and

R. These parameters are found to be related as follows. Consider a sequence of reactions,

$$A^+ + B^- \rightleftharpoons (A^+ \ldots\ldots B^-) \rightleftharpoons A^+B^- \qquad (24)$$

where $(A^+ \ldots\ldots B^-)$ denotes the configurations in which cation and anion are simultaneously in the volume $4\pi R^3/3$, separated by at least one solvent molecule ($a + S \leq \gamma \leq R$; S = diameter of solvent molecule).

The formation of diffusion pairs is described by

$$K_R = (1 - \gamma)(1 - \alpha) / C \gamma^2 f^2 \qquad (25)$$

and the formation of dipolar (contact) pairs by

$$K_S = \alpha / (1 - \alpha) \qquad (26)$$

The pairing constant, K_A (previously designated by K_A = association constant) is then given by

$$\begin{aligned} K_A &= (1 - \gamma)/C \gamma^2 f^2 \\ &= K_R / (1 - \alpha) \\ &= K_R (1 + K_S) \end{aligned} \qquad (27)$$

in which the subscript Λ indicates the conductometric origin of K_Λ, the subscript R indicates that K_R depends explicitly on the pairing distance, and the subscript S indicate that $K_S = \exp(-E_S / KT)$, which describes the short-range effects; as E_S and R both depend on the molecular parameters specific to cation and the solvent molecules. Therefore, this model does not imply an iso-dielectric rule and the erratic variation of K_Λ with dielectric constant do not arise. Fuoss has pointed out that his model demands at least a ten fold dilution of the solution, the maximum concentration being determined by the relation[49], $C_{max} = 2 \times D^3 \times 10^{-7}$ moles per liter where D refers to the dielectric constant of the solvent.

Kay, Kraus, Evans and Fuoss have shown a very keen interest in this area of studies[51-61]. They measured the electrical conductance of organic and inorganic electrolytes in various aqueous and non-aqueous solvents. Such results have recently been analyzed in terms of Fuoss-Hsia, Fuoss-Kraus and 1978-80 Fuoss equations[62-72]. In addition, Debye-Huckle-Onsager and Shedlovsky models were also employed[73] for the same purpose. However, such studies of tetra-alkyl ammonium salts in mixed solvents have drawn much attention[11, 14-23] because of the fact that these salts have good solubility characteristics in a large variety of binary solvents and also possesses a unique model electrolyte whose cation has a tetrahedral symmetry and their structure is described as a point charge embedded in sphere of

paraffin, while anion is spherical with charge uniformly distributed over the peripheral volume. Moreover, they form a homologous series, which facilitates the comparison in study.

It would be, therefore, interesting to undertake the analysis of conductance data of tetra-alkyl ammonium halides in terms of Fuoss 1978, Justice (J), Pitts (P) and Fuoss-Onsager-Skinner (FOS) equations in order to examine their applicability and the suitability of the relevant models to such systems. Such an attempt highlights the significance of 1978 Fuoss equation in understanding the behavior of electrical conductance of dilute electrolytic solutions in solvents of varied nature.

For this purpose, measurements of electrical conductances of tetra-alkyl (alkyl = methyl, ethyl, propyl and butyl) ammonium bromides in dioxane-water and ethylene glycol water mixtures of different dielectric constants covering the range from $10.71 \leq D \leq 69.69$ and $37.7 \leq D \leq 75.60$, respectively, have been made as a function of concentration at 25° C.

EXPERIMENTAL

CHEMICALS

Tetra-methyl ammonium bromide (Me_4NBr) [BDH, AG], tetra-ethyl ammonium bromide (Et_4NBr), tetra-propyl ammonium bromide (Pr_4NBr) [both Fluka, AG] and tetra-butyl ammonium bromide (Bu_4NBr) [Eastman, AG] were used as such for the conductivity measurements. 1, 4–Dioxane (BDH and E. Merck, AR) and ethylene glycol (Sarabhai) were used as solvents after further purification.

PURIFICATION OF SOLVENTS

(a) 1, 4–Dioxane[74]: 1, 4–Dioxane was refluxed with concentrated hydrochloric acid and distilled water for 12 hours while a slow stream of pure and dry nitrogen was bubbled through the solution. The cold solution was shaken with potassium hydroxide pellets and while some of them remained undissolved, the aqueous layer is run off. Most of the residual water was removed by keeping the dioxane over fresh potassium hydroxide pellets for two hours and then distilled and stored in an inert atmosphere of pure and dry nitrogen. The density (1.03029 $Kg.m^{-3}$) and viscosity (0.77866 cp) were found to agree with those of the reported values[75].

(b) Ethylene glycol[76]: Ethylene glycol was dried with anhydrous sodium sulphate and then fractionally distilled at 198° C (b.p. 194° –

199°). Pure ethylene glycol was stored in a well-fitted glass-stoppered bottle in an inert atmosphere of pure and dry nitrogen. The density (1.1013 $Kg.m^{-3}$), viscosity (0.1690 cp) and specific conductance (≥ 7 x 10^{-8} ohm^{-1} cm^{-1}) were found to agree with those reported earlier[76].

APPARATUS

(a) Temperature Control: A double walled thermo-stated water bath was used to maintain a uniform temperature. It consists of an immersion heater (250 V / 600 W), stirrer, one check thermometer and a contact thermometer [TGL 4850 NAV = 0.03 A Un = 250 V (GDR)]. The check thermometer (Germany) was N.B.S. calibrated to record ±0.1° variation. The temperature was controlled by a relay [Jumo-type, NT 15.0, 220V-15A (Germany)]. The stability in temperature as checked by Beckman thermometer was within ± 0.05°.

(b) Density: A calibrated pyknometer was used for the density measurements. The pyknometer consists of a glass bulb of 7.862 ml capacity fitted with graduated stem of 7.5 cm length and 2 mm diameter. The stem of pyknometer is graduated in 0.01 ml divisions so that the volume could be read up to 0.005 ml.

(c) Viscosity: Cannon-Ubbelohde viscometer[77] was used for the viscosity measurements.

(d) Conductance: An LCR bridge GR-1657 (general Radio 1982, Bolton, Massachusetts, U.S.A.) was used for the conductance measurements at a frequency of 1 kHz with an accuracy of ± 0.05 % to ± 0.005 %. The Pyrex conductivity cell was designed in such a manner so that it could record the conductance of small amounts of solutions.

METHODS

Preparation of Binary Solvent Mixtures:

The binary ethylene glycol-water mixtures of varying dielectric constants[78] under study were prepared by weight. Triply distilled water (sp. Conductance 2.5 x 10^{-6} ohm^{-1} cm^{-1}) was used for preparing different solvent mixtures. To obtain a mixture of desired mole fraction the calculated amounts of the components were mixed. The stock solutions of various compositions were kept capped in stoppered flasks in a dry atmosphere of nitrogen.

Preparation of Electrolytic Solutions:

All the electrolytic solutions were prepared by weight. The solute was weighed in a weighing bottle and was transferred to a 50 ml standard flask in a dry box in an inert atmosphere of pure and dry

nitrogen. Initially a concentrated electrolytic solution was prepared and solutions of different concentration were prepared by the method of dilution. The highest concentration was not allowed[48] to exceed, $2 \times D^3 \times 10^{-7}$ mol dm^{-3}.

Measurement of Density:

The clean and dried pyknometer was weighed and filled with the pure and distilled quinoline up to a definite mark on the graduated stem and again weighed. The difference of these two weights gave the weight of quinoline taken. Now the pyknometer was immersed in the thermo-stated water bath. The temperature of the thermostat was increased till the meniscus of quinoline coincided with the next higher mark. The temperature corresponding to each mark was recorded. In order to avoid the effect of air tension inside the pyknometer the cork was opened for a while at each reading. Thus all the marks on the stem of the pyknometer were calibrated at the corresponding temperatures. At these temperatures the densities of quinoline were calibrated by means of the equation[79].

$$\rho = 1.109 - 0.7542 \times 10^{-3} T - 0.1265 \times 10^{-6} T^2 - 0.80 \times 10^{-9} T^3$$

where ρ is the density of quinoline and T is the temperature at each mark on the stem of the pyknometer. Now the ratios of the amount of

quinoline to the above-calculated densities at the respective temperature gave the volumes of the pyknometer at the corresponding marks on the stem.

The same procedure was repeated with different amounts of quinoline. The observed densities on the basis of calibration were compared with those of the reported values[79]. It was found that the accuracy of density measurement was within ± 0.0016 %. Similarly, the density of the solvent and those of the electrolytic solutions were measured with the help of the calibrated pyknometer by recording the volume change as a function of temperature.

Measurement of Viscosity:

The viscometer was filled with pure and distilled quinoline and all the three arms were connected through rubber tubing to anhydrous calcium chloride tubes to avoid the absorption of moisture. The viscometer was clamped in a vertical position in the thermostat and allowed to stand for approximately forty-five minutes for the maintenance of the desired temperature. The sample was sucked into the viscometer with a vaccupet and after allowing ten minutes it was allowed to fall freely. The time of fall of the liquid was recorded. The reproducibility of the result was checked by repeating the same experiment several times. Similar measurements were made at different temperatures. From the reported values of the density and

viscosity[79] the viscometer constant, β, was calculated using the equation,

$\eta = \rho \beta t$, in which

$\beta = \pi h g \gamma^4 / (8 L V)$ of the Poiseuele's equation,

$\eta = \rho \pi h g \gamma^4 t / (8 L V)$.

The viscometer constant, β, was found to be 0.0023 cSt / sec. The accuracy of calibrated viscometer was checked by measuring the viscosity of toluene at test temperature and compared with those of the reported values[79]. The reproducibility was found to be within ±0.4%.

Measurement of Conductance:

The conductivity cell was calibrated by Lind's method[80] using aqueous solution of potassium chloride. The cell constant was found to be 0.854 cm^{-1}.

A known volume of the electrolytic solution was taken in the cell and immersed in a thermo-stated water bath maintained at 25° C. After 15 minutes the conductance of the solution was recorded. The

solutions of the lower concentration were obtained by dilution and the conductance values were recorded after attainment of thermal equilibrium. The solutions of approximately ten folds dilution were thus obtained. All the measurements were made in an inert atmosphere of pure and dry nitrogen.

Dielectric Constants[78]:

The reported dielectric constant values of the solvent mixtures were used in calculations.

CHAPTER I

STUDIES OF ELECTRICAL CONDUCTIVITY AND IONIC ASSOCIATION OF TETRA-ALKYL AMMONIUM - HALIDES IN 1, 4 DIOXANE WATER MIXTURES AT 25°C

RESULTS AND DISCUSSION

Densities and Viscosities of Solvent Mixtures

The densities, ρ and the viscosities, η of dioxane-water mixtures covering the dielectric constant range, $10.71 \leq D \leq 69.69$ have been measured as a function of weight percent (W %) of dioxane at 25° C and are listed in Table 1. The observed values of density and viscosity of dioxane are 1.03029 (Kg. m^{-3}), and 0.778669 (centipoise) respectively. These are found to be in good agreement with those of the reported values[75]. The densities of solvent mixtures are found to increase with an increase in the W % of dioxane at a dielectric constant value, D =17.69 corresponding to the 70 W % dioxane and then decrease with decrease in the dielectric constant of the medium. Similarly, the viscosity of the solvent mixtures also increases with decrease in the dielectric constant and reaching a maximum value at the dielectric constant, D = 17.69 and it further decreases with decrease in the dielectric constant as is evident from plots of η versus D (Fig. 1).

The Electrical Conductance:

The molar conductivity, Λ (S cm^2 mol^{-1}) of dilute solutions of Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in dioxane-water mixtures of

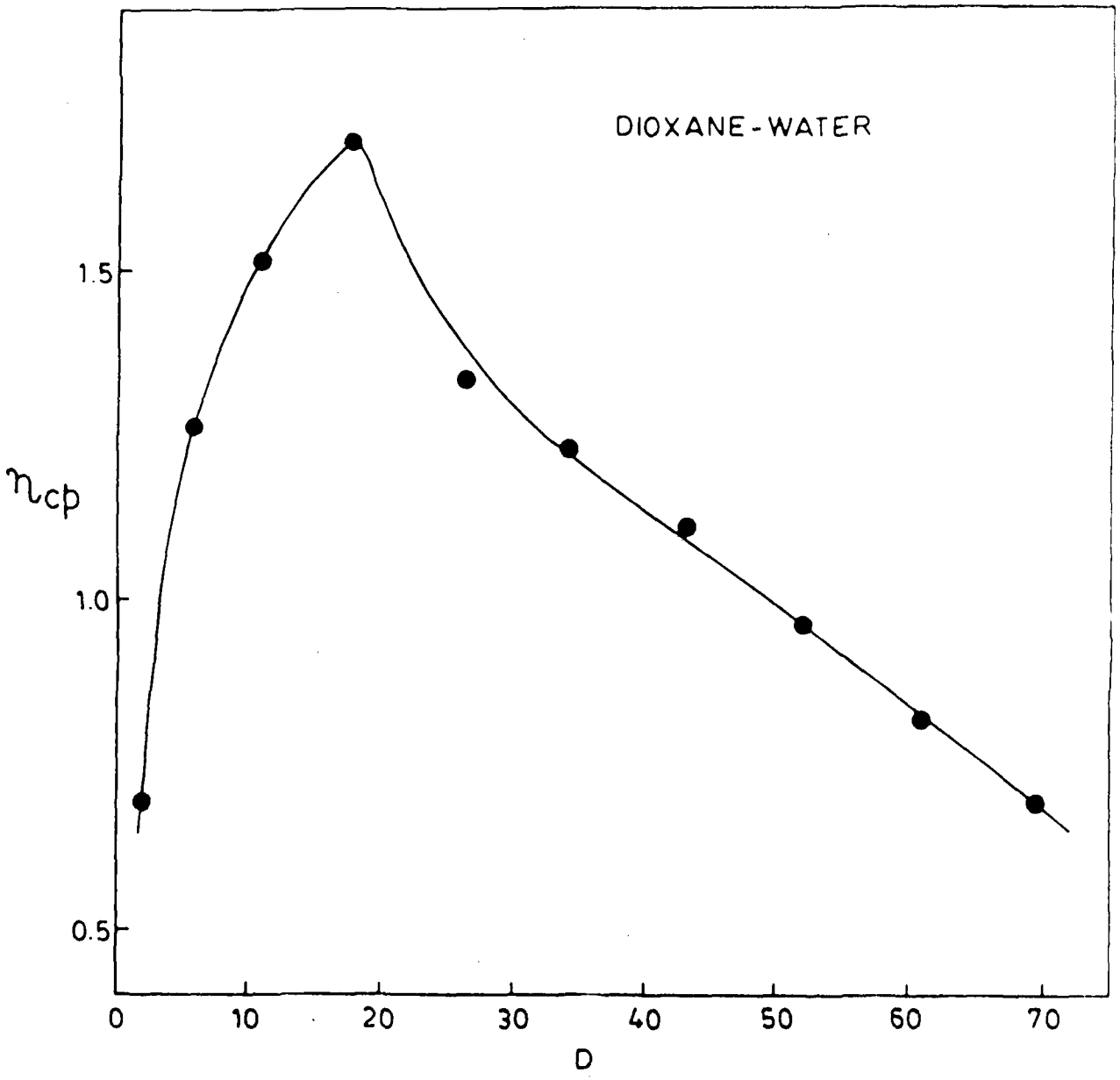

FIG. 1. VISCOSITIES OF DIOXANE-WATER MIXTURES AS A FUNCTION OF DIELECTRIC CONSTANT AT 25°C.

Table 1: Densities, ρ, viscosities, η and dielectric constant, D for Dioxane-water mixture at 25° C.

Dioxane W %	ρ (Kg m^{-3} x 10^3)	η (Kg $m^{-1}S^{-1}$ x 10^3)	D
10	1.00913	0.6932	69.69
20	1.01651	0.8256	60.79
30	1.02299	0.9685	51.90
40	1.03081	1.11523 (1.771)	42.98
50	1.03485	1.23381	34.26
60	1.03746	1.28677	25.85
70	1.03824	1.69618 (1.944)	17.69
80	1.03718	1.51182 (1.732)	10.71
90	1.03421	1.26607	05.60
100	1.03029 (1.0296)	0.77866	02.10

Reported values are given in parantheses[75].

varying dielectric constant values covering the range, $69.69 \geq D \geq 10.71$, have been measured at various concentrations, C (mol. dm^{-3}), at 25° C as listed in Table 2.

The electrical conductances of dilute solutions of all the salts under study are found to decrease with increase in the solute concentration as apparent from the Onsager plots of Λ against $\sqrt{C}$ (Figs. 2.1 to 2.8). Such a trend seems to be due to the presence of dynamic equilibrium between the free current carrying ions on the one hand and the non-conducting entities in the medium on the other. The relative concentration of the latter is increased with the increasing solute concentration resulting in a decrease in the Λ values. This behavior is also explainable in the light of the electrostatic theory, which considers a decrease in the equivalent conductance as due to the presence of long-range effects of electrostatic force of attraction between the ions and the dipoles, which become sufficiently strong to stabilize the ion-dipole pair as a kinetic unit. Consequently, the relaxation field, ΔX and the electrophoretic counter current, $\Delta\Lambda_e$ appear to result in the decrease in the equivalent conductance.

Table 2: Molar conductivities, Λ (S cm^2 mol^{-1}) and molar concentration C (mol dm^{-3}) of Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in dioxane water mixture at 25° C.

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			10 W % Dioxane				
374.00	89.159	339.70	96.901	411.30	85.316	409.40	90.888
305.20	93.136	292.00	99.550	352.00	87.996	345.20	93.202
235.40	98.132	225.30	103.956	283.50	91.647	297.50	95.150
183.40	102.762	182.60	107.245	196.60	97.702	204.30	99.775
105.60	112.110	112.00	114.535	153.20	101.300	152.10	103.046
92.40	114.155	98.30	116.256	95.30	107.727	104.30	106.755
83.40	115.960	87.50	117.730	87.20	108.818	94.20	107.660
71.30	117.845	75.30	119.520	79.50	109.905	72.80	109.673
64.20	119.226	64.20	121.308	69.35	111.442	65.30	110.593
58.50	120.400	59.20	122.155	60.52	112.875	53.20	112.032
50.30	122.195	51.50	123.545	54.32	113.970	48.50	112.632
47.20	122.914	47.80	124.155	48.23	115.092		
40.50	124.562	40.20	125.878				

Continued...

Table 2 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			20 W % Dioxane				
407.00	89.833	471.20	79.564	389.20	70.106	368.20	74.878
345.20	92.733	408.20	82.312	316.50	74.188	307.50	78.154
295.00	95.554	339.50	86.036	257.30	78.211	265.20	80.558
234.80	99.754	286.20	89.285	203.40	82.788	214.30	84.456
174.50	104.629	229.50	93.432	165.24	86.800	173.20	88.070
106.90	112.168	186.70	97.224	103.45	95.444	125.60	93.287
94.20	113.914	102.85	107.353	91.60	97.709	99.50	96.950
85.60	115.186	90.40	109.373	82.40	99.448	87.20	98.760
72.50	117.281	81.50	110.908	73.20	101.447	75.30	100.815
65.50	118.499	73.40	112.410	65.30	103.412	70.80	101.640
57.20	120.023	64.20	114.251	60.90	104.507	64.80	102.790
50.80	121.285	55.30	116.197	54.50	106.230	60.50	103.660
46.20	122.248	50.90	117.208	50.70	107.302	55.70	104.686
39.50	123.634	46.20	118.359	45.20	108.965	50.42	105.869
		40.80	119.763	40.20	110.474	46.30	106.740
		36.70	120.805	35.60	112.163	40.90	108.186
						36.20	109.442

Continued...

Table 2 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			30 W % Dioxane				
210.30	79.099	206.60	65.628	206.40	62.627	184.20	81.694
168.90	82.425	158.60	69.873	157.60	66.736	151.45	83.574
129.20	86.350	134.82	72.449	133.40	69.256	130.54	84.943
95.40	90.594	108.25	75.896	109.52	72.180	106.56	86.694
85.20	92.034	95.42	77.835	99.32	73.615	96.49	87.531
76.30	93.430	86.53	79.317	88.92	75.214	87.05	88.336
68.90	94.693	78.32	80.807	77.53	77.144	76.82	89.302
59.20	96.470	69.54	82.534	68.50	78.758	67.42	90.233
48.60	98.650	59.32	84.766	57.40	81.199	58.39	91.225
42.50	100.035	49.63	87.187	48.52	83.326	49.82	92.136
37.50	101.252	42.56	89.152	43.51	84.655	45.72	92.766
32.95	102.440	39.68	90.023	40.23	85.636	40.15	93.504
24.56	104.869	35.48	91.344	36.71	86.621	35.67	94.154
		31.89	92.573	32.54	87.945	31.81	94.743
		27.46	94.199	30.45	88.651	26.84	95.547
				28.54	89.310	23.82	96.075
				24.94	90.770		

Continued...

Table 2 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			40 W % Dioxane				
156.80	63.480	153.70	60.587	130.16	57.313	137.15	61.046
109.78	67.326	130.04	62.339	105.67	59.475	109.95	62.859
94.58	68.873	108.50	64.187	94.20	60.644	97.52	63.800
78.24	70.766	92.40	65.777	83.20	61.881	86.43	64.726
69.34	71.924	86.71	66.395	72.39	63.221	71.95	66.085
60.75	73.133	75.42	67.719	65.31	64.203	64.85	66.817
52.74	74.395	68.45	68.615	60.25	64.941	60.15	67.327
45.63	75.616	60.53	69.701	54.83	65.794	53.72	68.086
40.38	76.606	55.62	70.440	46.52	67.210	46.92	68.947
36.24	77.438	48.75	71.530	40.25	68.403	40.87	69.763
32.62	78.215	40.56	72.984	34.51	69.602	33.84	70.827
29.54	78.922	35.72	73.923	29.85	70.673	28.50	71.723
26.92	79.555	31.84	74.738	25.56	71.842	26.35	72.121
22.32	80.737	27.54	75.705	21.98	72.712	19.23	73.520
19.52	81.530	23.78	76.621	18.52	73.730	15.37	74.396
16.98	82.292	19.86	77.766	15.42	74.730	12.75	75.051
14.52	83.089	16.92	78.526	12.85	75.637		
		13.92	79.336				

Continued...

Table 2 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			50 W % Dioxane				
83.084	53.585	80.087	53.568	72.557	48.960	65.290	49.732
71.520	55.070	71.324	54.708	61.742	50.502	52.450	51.754
60.840	56.635	60.540	56.306	49.520	52.558	40.790	53.998
51.450	58.235	48.650	58.377	39.780	54.533	34.720	55.380
39.850	60.567	36.560	60.485	29.980	56.952	27.960	57.155
26.750	63.945	28.310	63.113	21.850	59.461	20.950	59.354
19.950	66.164	20.750	65.523	15.970	61.695	16.150	61.162
15.950	67.706	15.850	67.402	13.050	62.995	12.880	62.582
12.680	69.136	12.832	68.731	10.950	64.035	10.580	63.709
9.867	70.533	9.962	70.159	8.985	65.111	9.142	64.482
8.639	71.211	8.752	70.817	7.782	65.835	8.065	65.096
7.842	71.674	7.351	71.645	6.539	66.625	6.572	66.115
6.483	72.507	6.273	72.333	5.432	67.396	5.237	66.935
5.138	73.415	5.364	72.955	4.423	68.152	4.175	67.732
4.480	73.885	4.523	73.567	3.852	68.634	3.554	68.232
3.851	74.370	3.989	73.977				

Continued...

Table 2 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			60 W % Dioxane				
34.540	40.632	33.980	44.840	31.560	46.020	34.150	48.640
26.950	43.092	25.860	47.234	22.950	48.214	23.560	50.865
20.850	45.628	20.730	49.092	19.870	49.371	18.952	52.083
17.540	47.301	18.950	49.852	15.860	50.880	16.532	52.805
14.530	49.115	16.350	51.055	13.780	51.853	13.782	53.725
10.950	51.728	10.950	54.097	10.240	53.549	10.150	55.153
9.070	53.390	9.020	55.445	8.750	54.315	8.625	55.825
7.830	54.627	8.170	56.133	7.250	55.345	7.024	56.632
6.450	56.192	6.870	57.196	6.245	56.060	5.983	57.202
5.230	57.760	5.780	58.116	5.052	57.087	5.045	57.768
4.760	58.445	4.950	59.078	4.365	57.566	4.595	58.063
3.790	59.963	3.870	60.293	3.275	58.590	3.554	58.780
2.870	61.601	2.790	61.696	2.384	59.542	2.754	59.403
2.230	62.910	2.340	62.362	1.926	60.084	2.341	59.750
		2.070	62.763				

Continued...

Table 2 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			70 W % Dioxane				
11.076	39.240	10.790	41.512	11.052	38.529	11.025	36.680
8.245	40.795	8.754	42.610	8.465	39.962	8.649	37.886
7.014	41.686	7.975	43.092	7.685	40.498	7.284	38.794
5.842	42.715	6.854	43.891	6.642	41.322	6.581	39.354
5.075	43.516	6.037	44.573	6.013	41.896	5.894	39.668
3.972	44.932	5.246	45.324	5.345	42.575	4.972	40.940
2.864	46.842	4.078	46.698	4.567	43.495	4.078	42.109
2.486	47.674	3.281	47.883	3.945	44.364	2.583	42.877
1.957	49.045	2.574	49,203	3.079	45.842	2.964	44.028
1.685	49.900	2.279	49.859	2.585	46.894	2.436	45.215
		1.974	50.630	2.098	48.126	1.986	46.472
		1.537	51.910	1.884	48.755	1.775	47.150
				1.579	49.781	1.569	47.890
				1.465	50.207		

Continued...

Table 2 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			80 W % Dioxane				
2.456	31.371	2.423	30.421	2.379	29.934	2.426	31.241
1.952	32.167	2.074	30.927	2.086	30.353	2.089	31.612
1.685	32.650	1.882	31.330	1.854	30.730	1.863	31.870
1.450	33.117	1.692	31.565	1.702	30.974	1.718	32.056
1.335	33.373	1.567	31.790	1.590	31.172	1.578	32.240
1.198	33.669	1.385	32.151	1.450	31.436	1.437	32.452
1.057	34.058	1.069	32.848	1.280	31.758	1.259	32.725
		0.956	33.131				

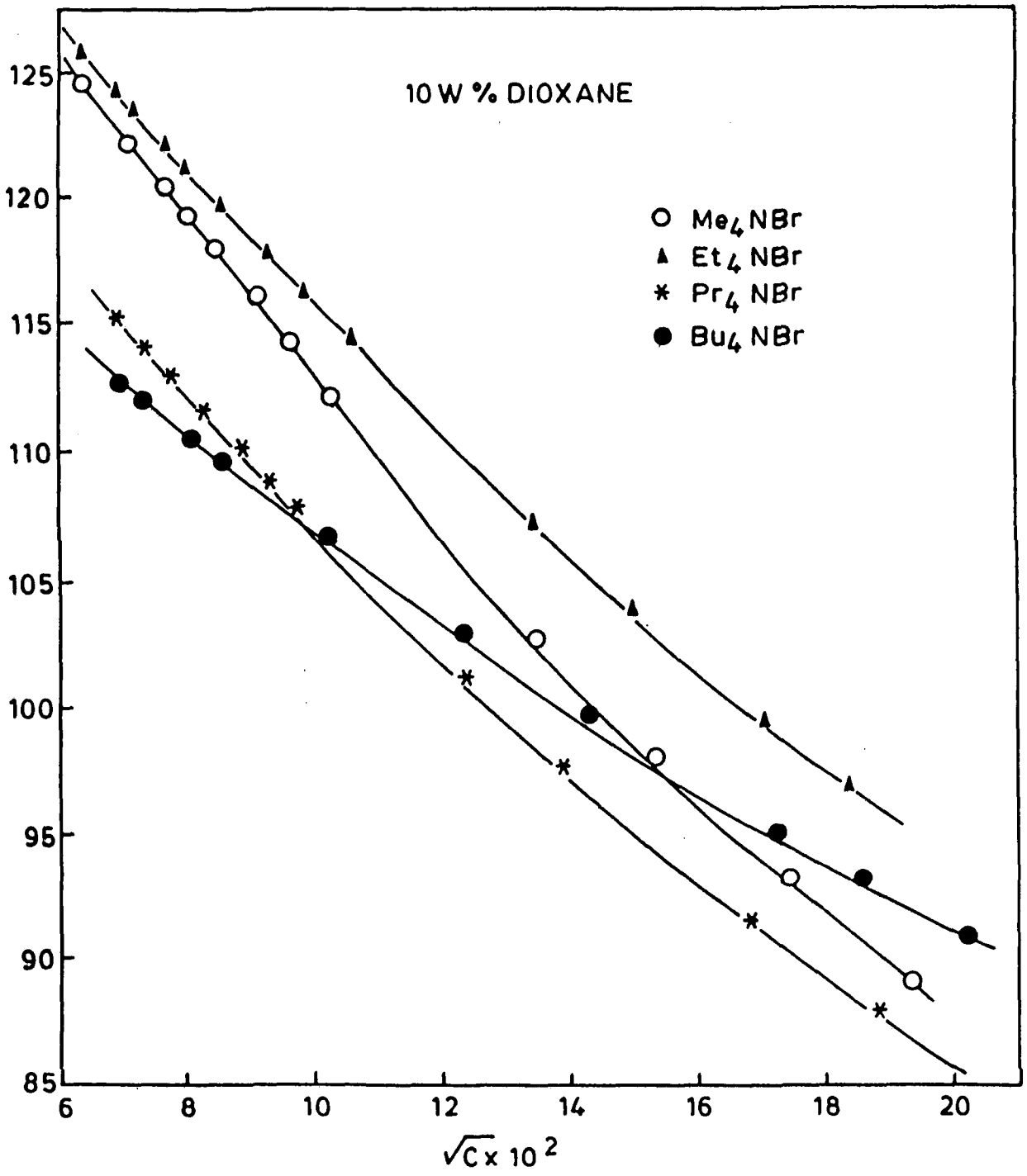

FIG. 2.1. ONSAGER PLOTS OF Me_4NBr, Et_4NBr, Pr_4NBr AND Bu_4NBr IN DIOXANE-WATER MIXTURES AT 25°C.

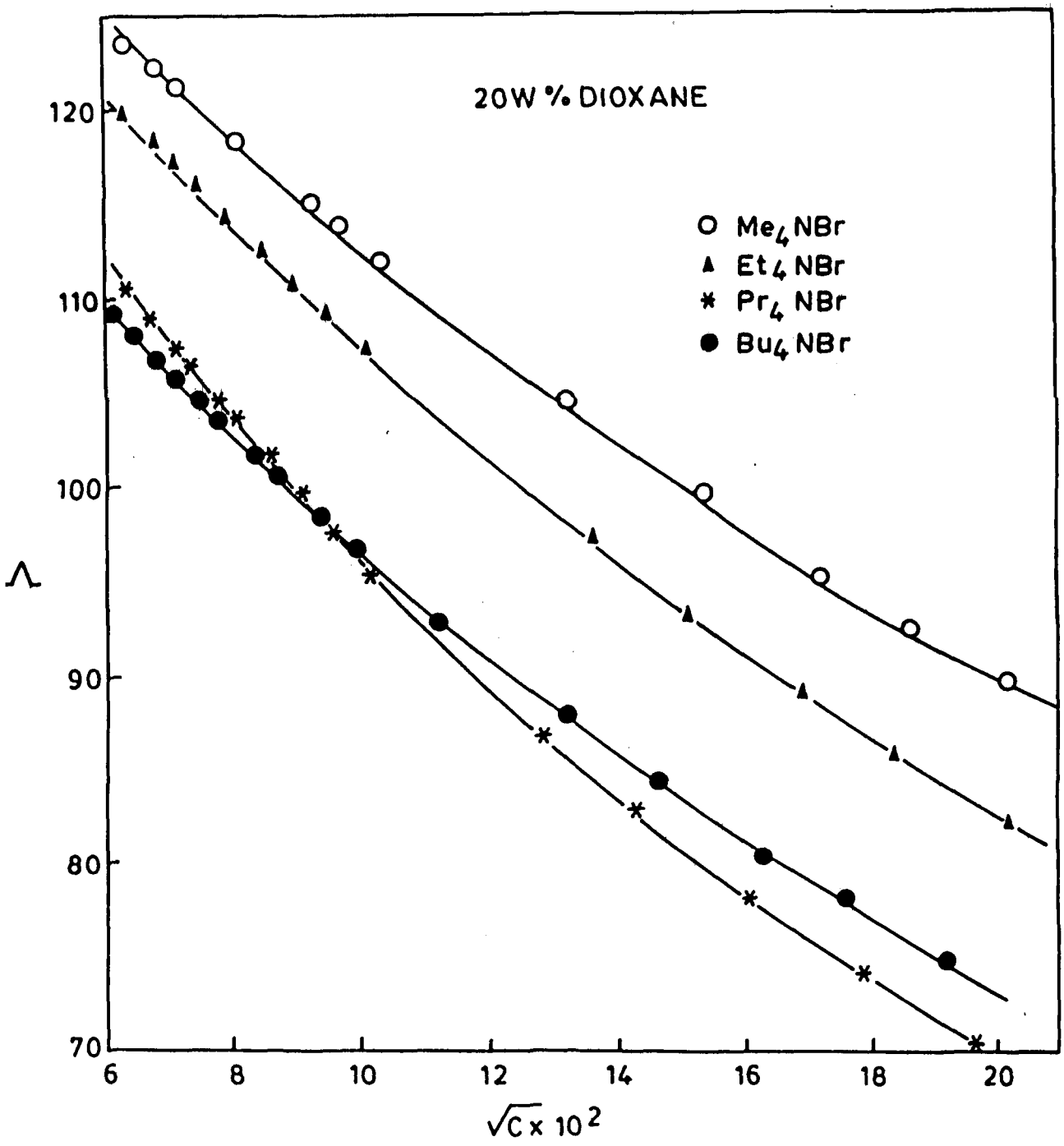

FIG. 2.2. ONSAGER PLOTS OF Me_4NBr, Et_4NBr, Pr_4NBr AND Bu_4NBr IN DIOXANE-WATER MIXTURES AT 25°C.

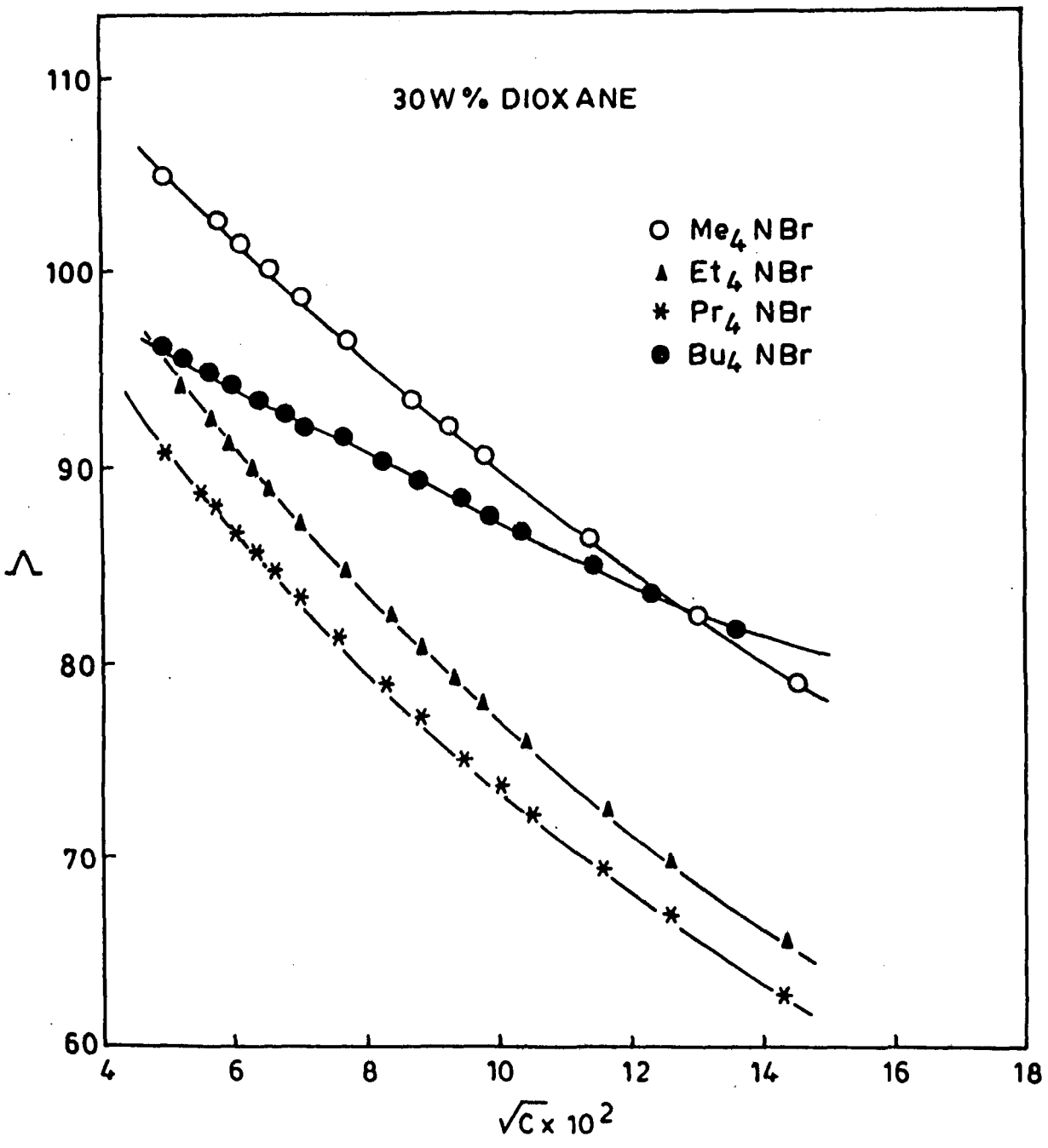

FIG. 2.3. ONSAGER PLOTS OF Me_4NBr, Et_4NBr, Pr_4NBr AND Bu_4NBr IN DIOXANE-WATER MIXTURES AT 25°C.

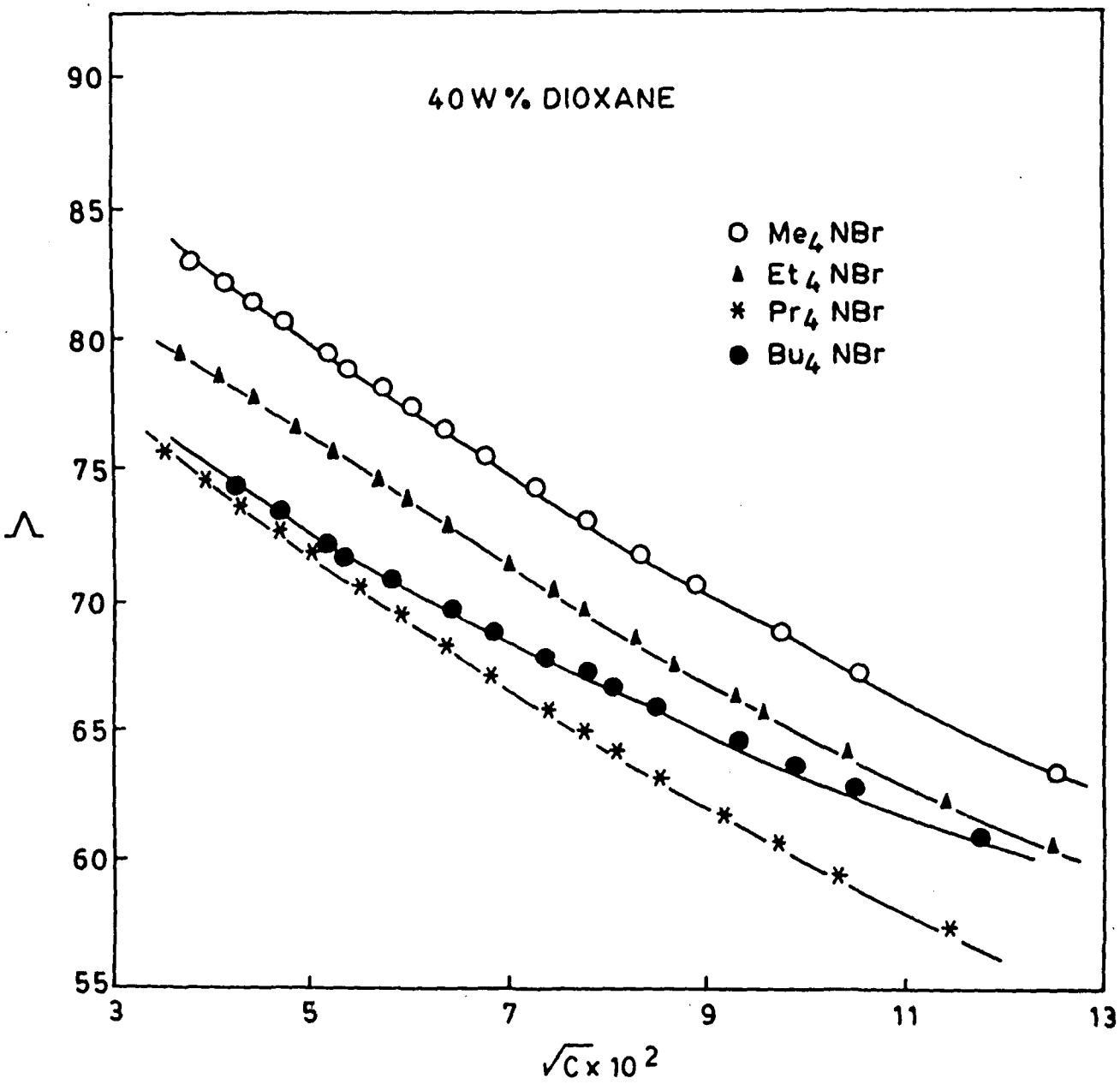

FIG. 2.4. ONSAGER PLOTS OF Me_4NBr, Et_4NBr, Pr_4NBr AND Bu_4NBr IN DIOXANE-WATER MIXTURES AT 25°C.

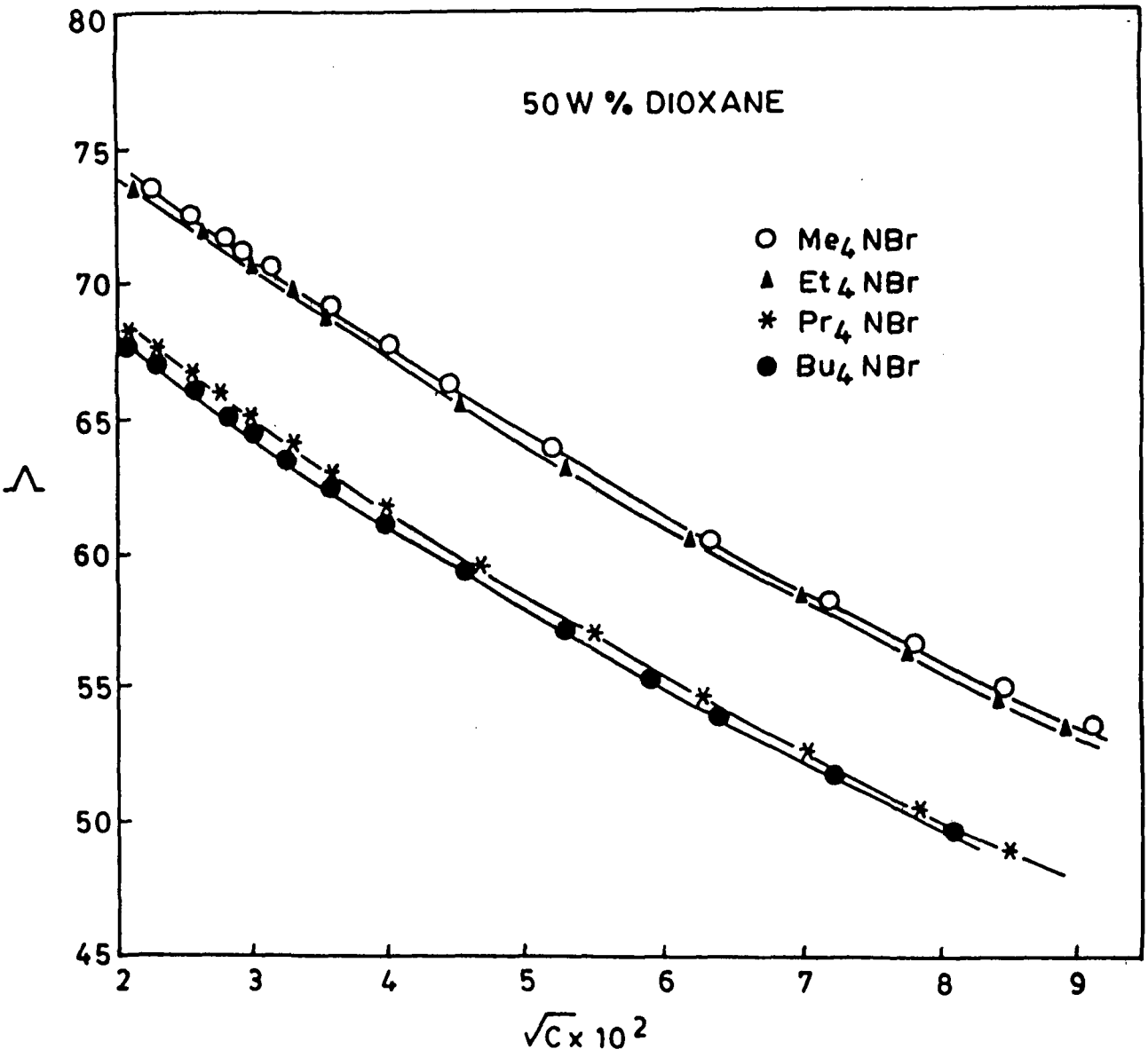

FIG. 2.5 . ONSAGER PLOTS OF Me_4NBr, Et_4NBr, Pr_4NBr AND Bu_4NBr IN DIOXANE-WATER MIXTURES AT 25°C.

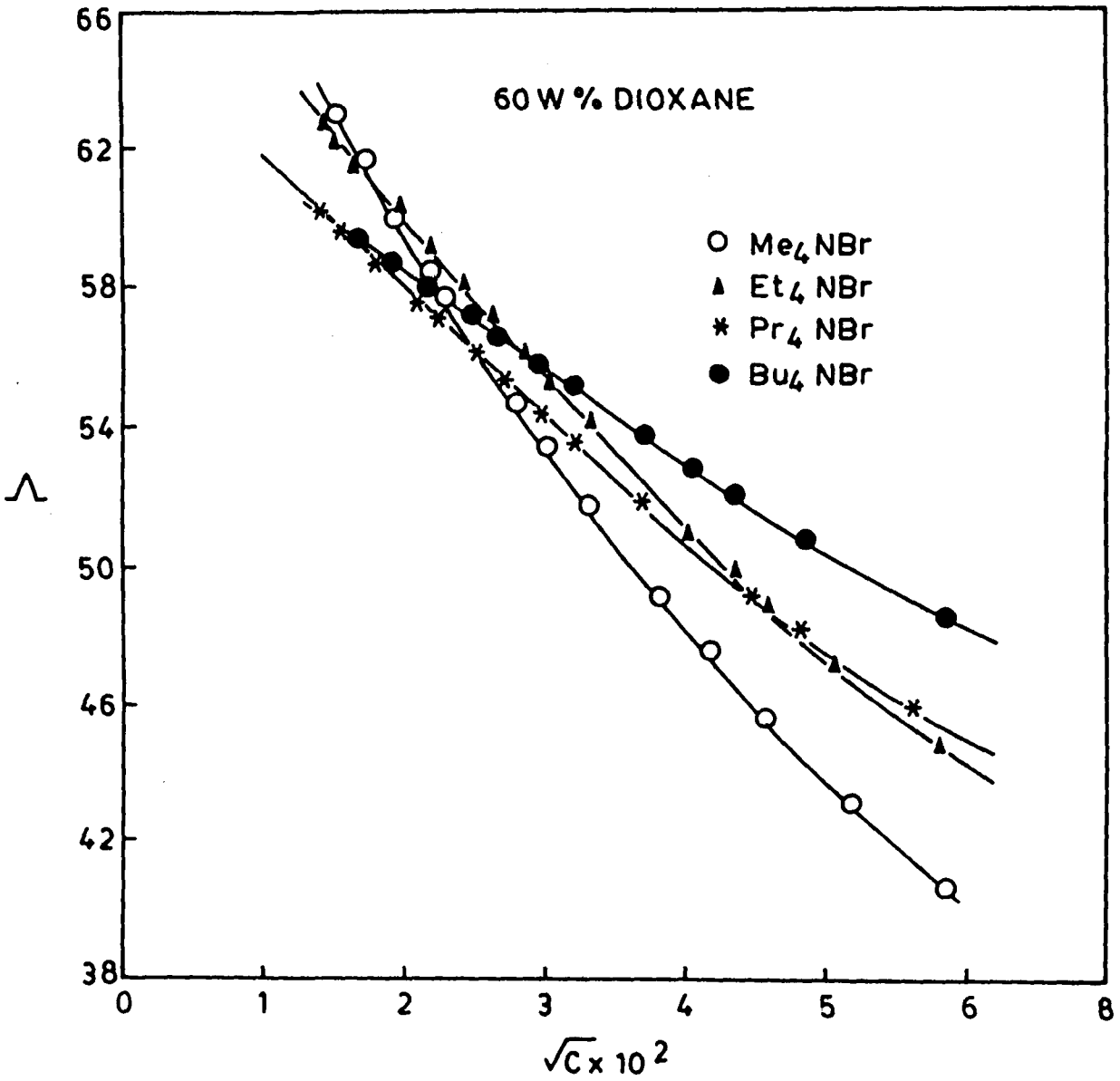

FIG. 2.6. ONSAGER PLOTS OF Me_4NBr, Et_4NBr, Pr_4NBr AND Bu_4NBr IN DIOXANE-WATER MIXTURES AT 25°C.

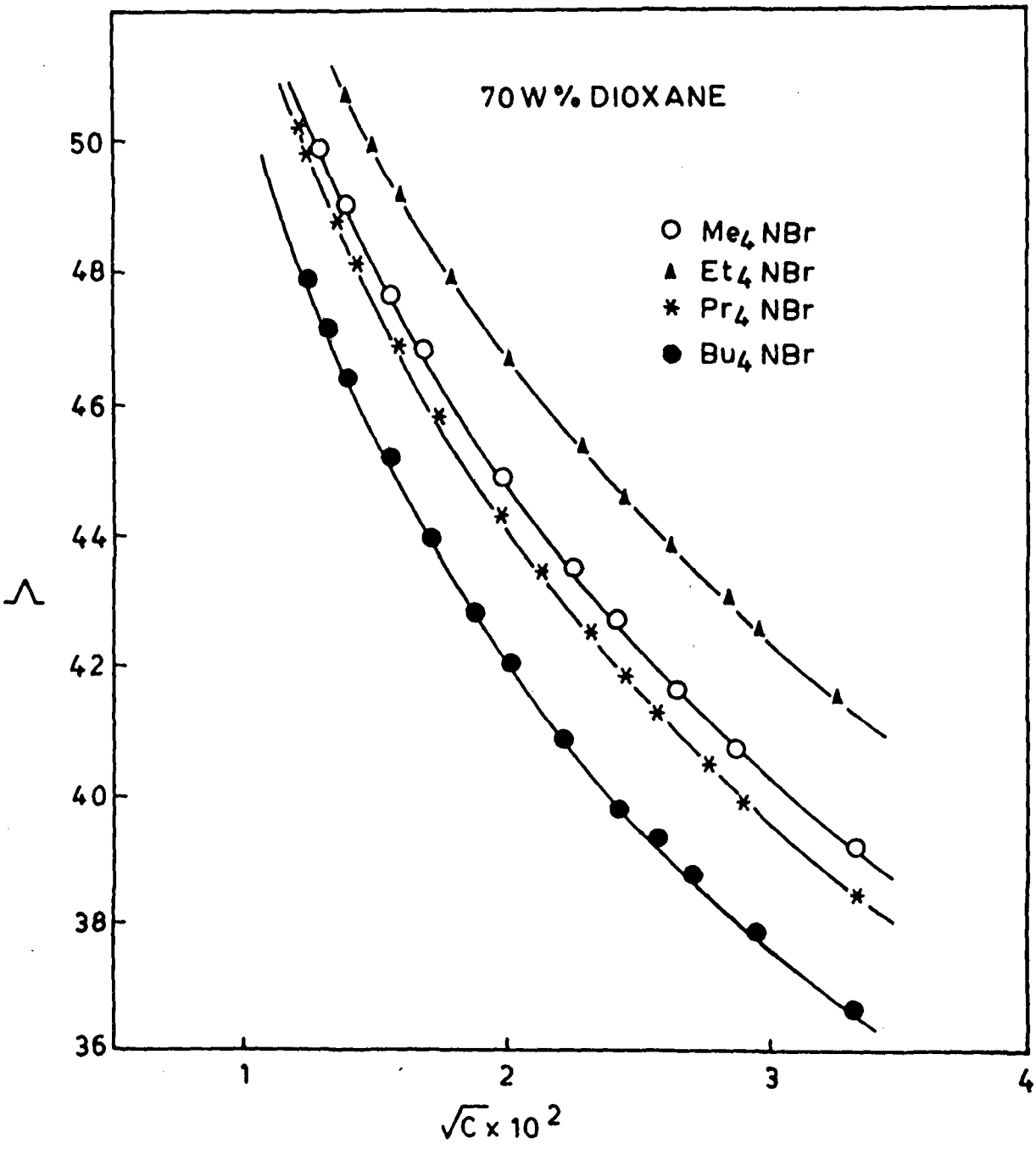

FIG. 2.7. ONSAGER PLOTS OF Me_4NBr, Et_4NBr, Pr_4NBr AND Bu_4NBr IN DIOXANE-WATER MIXTURES AT 25 °C.

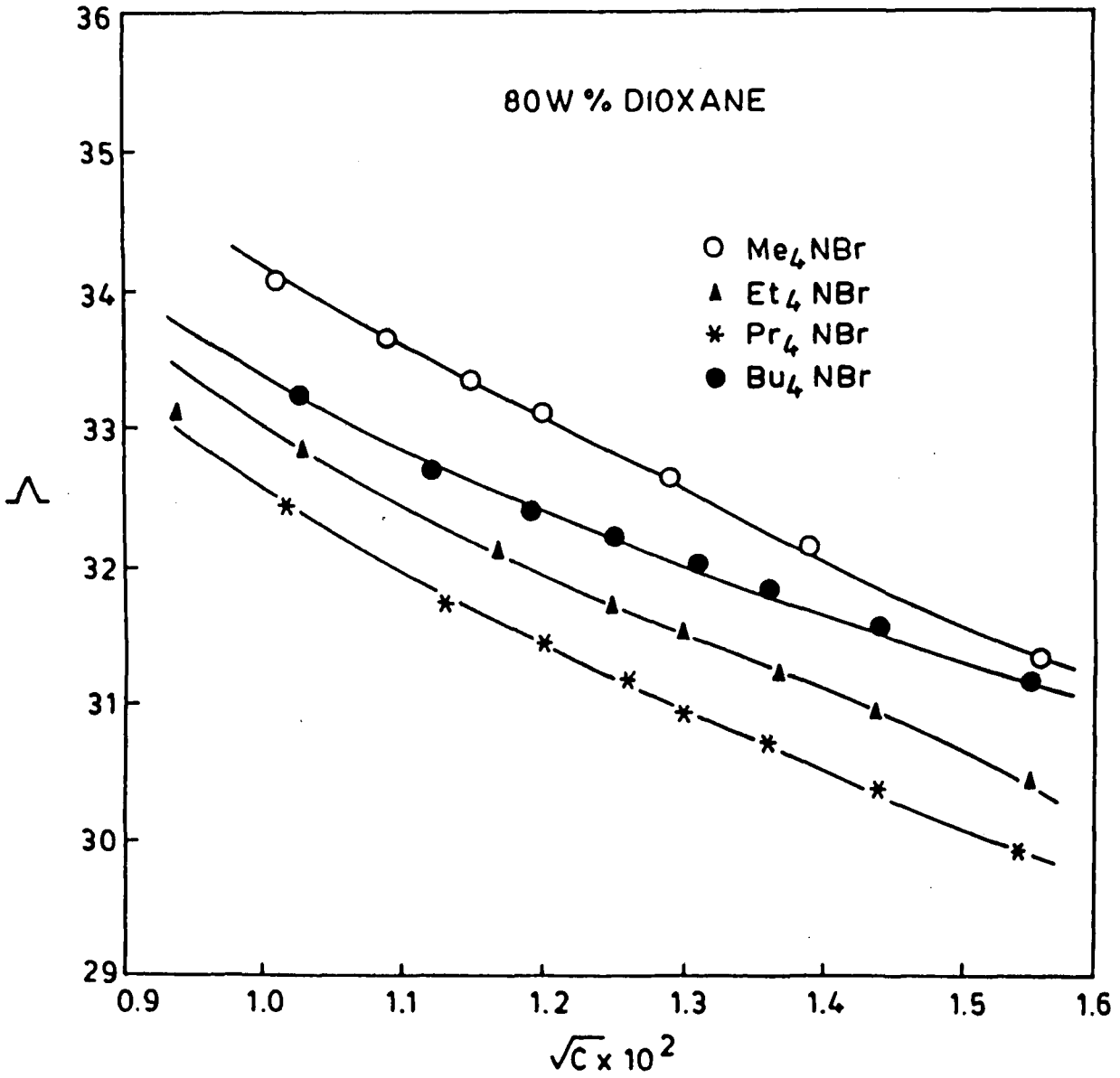

FIG. 2.8. ONSAGER PLOTS OF Me_4NBr, Et_4NBr, Pr_4NBr AND Bu_4NBr IN DIOXANE-WATER MIXTURES AT 25°C.

For a given dielectric the conductances of all the quarternary ammonium salts vary consistently with increasing size of the cation and therefore follow the order $Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$. It may be noted that the Me_4N^+ ion seems to be more mobile than Et_4N^+, Pr_4N^+ and Bu_4N^+ ions and this may be attributed to its smaller size as compared to those of the latter three ions. However, smaller the number of alkyl groups present in a given tetra-alkyl-ammonium ion greater will be the mobility. Similar results have also been observed in the study of conductance of tetra-alkyl-ammonium salts in pure and non-aqueous solvent mixtures[17, 81, 82]. The conductance of a given salt decreases with decreasing dielectric constant of the medium due to the formation of ion-dipole pair in dipolar protic and aprotic associated solvents as is observed in the present case.

Analysis of Conductance Data:

The concentration dependence of conductance data for all the salts have been first analyzed in terms of F78 conductance equation[48, 49] and compared with those analyzed by using FOS, J and P equations[83, 84, 85]. The F78 conductance equation[48, 49] based on the concept of diffusion controlled steady state approach is of the form,

$$\Lambda = [1 - \alpha (1 - \gamma)] [\Lambda_0 (1 + RX) + EL] \qquad (1.1)$$

where Λ_0 is the limiting equivalent conductance, the RX represents the relaxation effects, EL, the electro-phoretic effect or the hydrodynamic effect, γ represents the fraction of solute present as free ions and α is the contact pair parameter. Both the relaxation and the hydrodynamic terms depend on the values of the diameter of Gurney cosphere[86], R, the dielectric constant and the viscosity of the medium. These parameters are related as follows:

$$K_R = (1 - \alpha)(1 - \gamma) / C \gamma^2 f^2$$
$$= (4 \pi N R^3 / 3000) \exp(\beta / R) \qquad (1.2)$$
$$K_S = \alpha / (1 - \alpha) = \exp(-E_S / KT) \qquad (1.3)$$

where K_R denotes the formation and the separation constants of solvent separated ion-pairs by diffusion in and out of spheres of diameter, R, around the cations and K_S is the contact ion pair formation constant, which described the short-range process in which dipolar pairs form and dissociate, f is the activity coefficient, and E_S is the energy difference between a pair, when (r = R) and (r = a) where r is the center-to-center distance in paired ions and a is the ionic diameter. After rearranging equation (1.3), we get,

$$(1 - \alpha) = 1 / (1 + K_S) \qquad (1.4)$$

On substituting equation (1.4) into eqn. (1.2), the association constant, K_A, is given as,

$$K_A = (1 - \gamma) / C \gamma^2 f^2$$
$$= K_R / (1 - \alpha)$$
$$K_A = K_R (1 + K_S) \qquad (1.5)$$

while the activity coefficient, f, is given by

$$- \ln f = \beta \kappa / 2 (1 + \kappa R) \qquad (1.6)$$

where $\beta = e^2 / DKT$ and $\kappa = 8 \pi \beta \gamma n = \pi \beta N C \gamma / 125$.

Therefore, specially designed PARACOND[50] computer program for the PARAmetic analysis of conductance data for 1:1 electrolytes has been used. The equations (1.1 to 1.6) were used for the associated electrolytes to determine the values of the conductance parameter, Λ_0, K_A and R, when $\gamma < 1$ and $K_A > 0.0$, which minimize the standard deviation, σ_Λ, calculated from the following relation,

$$\sigma_\Lambda = [\Sigma \{\Lambda_{(obs)} - \Lambda_{(cal)}\}^2 / (N - 3)]^{1/2} \qquad (1.7)$$

Similarly, each set of conductance data has been analyzed using Justice's modification[84] of Fuoss Hsia[30] equation,

$$\Lambda = \gamma\,[\Lambda_0 - S\,(C\gamma)^{1/2} + EC\,\gamma \ln (C\gamma) + JC\,\gamma + J_{3/2}\,(C\gamma)^{3/2}] \qquad (1.8)$$

and

$$K_A = (1 - \gamma) / C\gamma^2\, f_{\pm}^2 \qquad (1.9)$$

where γ is the degree of dissociation, $f_{\pm}$ is the mean molar activity coefficient, and all the other terms have their usual significance.

The activity coefficients have been calculated from the Debye-Huckel equation,

$$\ln f_{\pm} = -A\,(\gamma C)^{1/2} / \{1 + BR_j\,(C\gamma)^{1/2}\} \qquad (1.10)$$

The distance parameter, R_j in eqn. (1.10) has been taken as the Bjerrum distance, q[84]. The calculation from J equation has been carried out by a pit-mapping method[87].

The set of conductance data analysed using F78, and J equations have also been analysed using Pitt's (P) equation[33, 85],

$$\Lambda = [\Lambda_0 - \frac{Z^2e^2\kappa}{(1+\kappa a)}(\frac{N10^9}{3\pi\eta_0 C^2})][1 - \frac{Z^2e^2\kappa}{3DKT(1+\sqrt{2})(1+\kappa a)(\sqrt{2}+\kappa a)}]$$

$$- \frac{Z^2e^2\kappa}{3D^2K^2T^2}[\Lambda_0 S_1 - \frac{T_1}{(1+\kappa a)}(\frac{NDKT10^9}{3\pi\eta_0 C^2})] \qquad (1.11)$$

$q = Z^2 e^2 \kappa / (DKT)$, $\kappa^2 = 8 \pi n Z^2 e^2 / (DKT)$ and

n = Number of positive and negative charges.

N is the Avogadro's number, η_0 is the solvent viscosity, C is the velocity of light, a is the ion-size parameter, and other symbols have their usual meaning.

Similarly, each set of conductance data was then analyzed by using FOS equation[83],

$$\Lambda = \Lambda_0 - SC^{1/2} + EC \log (6 E_1'C) + LC \qquad (1.12)$$

for unassociated electrolytes, while

$$\Lambda = \Lambda_0 - S (C\gamma)^{1/2} + EC \gamma \log (6 E_1'C\gamma) + LC\gamma - K_A C\gamma f_\pm^2 \Lambda_0 \qquad (1.13)$$

for associated electrolytes. The symbols used have their usual significance. For equations (1.12) and (1.13) a similar computer program was used as suggested by R.L. Kay[88, 89].

This initial values of the limiting equivalent conductance used in the Fuoss method of analysis have been obtained from those of the

Shedlovsky's method[28] of extrapolation of conductance data by least-squares. The values of Λ_0 have been computed for each of the sequence of R values by minimizing the standard deviation, σ_Λ. The computed values[49] of R, depend on the dielectric constant of the medium. It is initially set equal to $\underline{a}$ + $\underline{d}s$, where $\underline{a}$ is the sum of the crystallographic radii and $\underline{d}s$ is the diameter of a solvent molecule, when ($\underline{a}$ + $\underline{d}s$) is greater than $\beta/2$. When $\beta/2$ is greater than ($\underline{a}$ + $\underline{d}s$), R is set equal to $\beta/2$, $\beta/2$ values are used to find the value of R_{min} for each of the salts in order to obtain the final value of R.

The values of the best fit parameters of the limiting molar conductance, Λ_0, association constant, K_A, solvent separated ion-pair formation constant, K_R, contact ion-pair formation constant, K_S and the distance parameter, R, or ion-size parameter, a°, along with σ_Λ % (i.e. σ_{min} x 100 / Λ_0) thus computed which correspond to minimum standard deviation from F78, J, P and FOS conductance equations are listed in Tables 3-I, 3-II, 3-III and 3-IV, respectively.

Limiting Equivalent Conductance

A comparison of different available conductance equations has been made in respect of their applicability to the measured conductances. The computed values of Λ_0 obtained for all the salts through the F78 and J methods of treatment of conductance data are

found to be almost close to each other with an average deviation of ~ ± 0.032 % while those obtained by using the P and FOS conductance equations show ~ ± 0.15 % and ~ + 0.05 % deviations, respectively. An inspection of Table 3 (I – IV) reveals an apparently normal behavior of tetra-alkyl-ammonium salts in various solvent mixtures, i.e., Λ_0 decreases with increasing size of the tetra-alkyl-ammonium ions in the order $Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$ and with decreasing dielectric constant of the solvent mixtures which resemble those of their corresponding Λ values. This is in agreement with the earlier findings[17, 85, 90 - 99] in several pure and mixed solvents and this can be attributed to the size and the hydrophobic solvation of cations which increase in the order $Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+$, so that the mobility decreases in the reverse order. However, in any given solvent mixture the limiting equivalent conductance decreases in the order $Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$. Thus an overall decrease in Λ_0 values may be visualized in the light of the Walden product, $\Lambda_0\eta$.

Walden product

The values of the Walden product, $\Lambda_0\eta$ (Table 4) for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr solutions have been taken into consideration in order to understand the magnitude of conductance behavior in terms of the ion-solvent interactions. The plot of $\Lambda_0\eta$ versus 1 / D (Fig. 3) shows that the $\Lambda_0\eta$ passes through two sharp

Table 3 – I: **Best-fit parameters for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in dioxane-water mixtures at 25° C, using the F78 conductance equation.**

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	K_R	K_S	α Alpha	R A°	σ_Λ %
			10 W % Dioxane				
Me_4NBr	140.97 ± 0.07	27.65	2.14	11.92	0.9226	6.10	0.06
Et_4NBr	139.66 ± 0.04	23.63	3.89	5.06	0.8352	8.40	0.03
Pr_4NBr	130.29 ± 0.01	23.86	3.19	6.47	0.8663	7.60	0.01
Bu_4NBr	123.81 ± 0.02	14.39	3.19	3.51	0.7784	7.60	0.03
			20 W % Dioxane				
Me_4NBr	138.66 ± 0.04	25.87	2.59	8.96	0.8997	6.10	0.04
Et_4NBr	137.60 ± 0.05	34.67	2.72	11.72	0.9214	6.30	0.05
Pr_4NBr	132.89 ± 0.05	54.33	2.79	18.45	0.9486	6.40	0.04
Bu_4NBr	125.53 ± 0.05	37.37	2.65	13.05	0.9288	6.20	0.05

Continued...

Table 3 – I continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	K_R	K_S	α Alpha	R A°	σ_A %
			30 W % Dioxane				
Me_4NBr	117.15 ± 0.01	41.13	3.72	10.04	0.9095	6.60	0.01
Et_4NBr	111.47 ± 0.01	70.90	4.13	16.16	0.9417	7.10	0.01
Pr_4NBr	106.37 ± 0.04	74.55	5.98	11.45	0.9197	8.90	0.03
Bu_4NBr	103.64 ± 0.02	24.35	6.48	2.75	0.7339	9.30	0.02
			40 W % Dioxane				
Me_4NBr	91.01 ± 0.00	49.14	5.48	7.96	0.8884	6.90	0.005
Et_4NBr	86.93 ± 0.02	49.51	5.48	8.03	0.8893	6.90	0.03
Pr_4NBr	83.25 ± 0.02	58.73	5.15	10.40	0.9123	6.50	0.03
Bu_4NBr	80.76 ± 0.00	33.75	4.99	5.75	0.8519	6.30	0.01
			50 W % Dioxane				
Me_4NBr	79.06 ± 0.02	103.96	8.46	11.28	0.9186	6.30	0.005
Et_4NBr	78.79 ± 0.01	112.04	10.75	9.42	0.9041	8.60	0.01
Pr_4NBr	73.44 ± 0.01	128.62	10.10	11.73	0.9215	8.10	0.01
Bu_4NBr	72.74 ± 0.01	129.53	11.78	9.99	0.9091	9.30	0.03

Continued...

Table 3 – I continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	K_R	K_S	α Alpha	R A°	σ_Λ %
			60 W % Dioxane				
Me_4NBr	70.01 ± 0.01	470.79	20.07	22.45	0.9574	8.70	0.01
Et_4NBr	67.66 ± 0.02	283.23	19.13	13.80	0.9324	7.40	0.04
Pr_4NBr	63.86 ± 0.04	202.36	19.23	9.52	0.9050	7.70	0.09
Bu_4NBr	63.19 ± 0.01	130.47	19.56	5.66	0.8580	8.20	0.01
			70 W % Dioxane				
Me_4NBr	57.08 ± 0.02	644.99	64.37	9.02	0.9002	8.50	0.03
Et_4NBr	55.71 ± 0.06	741.63	66.23	10.19	0.9107	8.20	0.08
Pr_4NBr	55.69 ± 0.03	824.86	70.47	10.70	0.9146	7.70	0.06
Bu_4NBr	54.03 ± 0.02	908.14	69.49	12.06	0.9235	7.80	0.03
			80 W % Dioxane				
Me_4NBr	39.27 ± 0.03	1515.87	275.43	4.50	0.8183	15.40	0.03
Et_4NBr	37.76 ± 0.08	1406.04	303.37	3.63	0.7842	13.30	0.09
Pr_4NBr	37.07 ± 0.04	1403.71	315.35	3.45	0.7753	12.80	0.02
Bu_4NBr	36.89 ± 0.01	903.02	274.09	2.29	0.6965	15.60	0.01

Table 3–II: Best–fit parameters for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in dioxane-water mixtures at 25° C, using the Justice conductance equation.

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	R_j A°	σ_Λ %
		10 W % Dioxane		
Me_4NBr	140.77 ± 0.10	23.48	0.78	0.06
Et_4NBr	139.52 ± 0.05	16.97	-18.36	0.03
Pr_4NBr	130.07 ± 0.01	17.92	-18.69	0.01
Bu_4NBr	123.69 ± 0.03	8.73	2.64	0.02
		20 W % Dioxane		
Me_4NBr	138.40 ± 0.06	21.02	3.56	0.03
Et_4NBr	137.02 ± 0.06	28.58	3.72	0.03
Pr_4NBr	132.49 ± 0.08	48.14	1.84	0.04
Bu_4NBr	125.16 ± 0.07	31.72	3.17	0.04
		30 W % Dioxane		
Me_4NBr	117.02 ± 0.01	34.78	3.96	0.01
Et_4NBr	111.24 ± 0.01	62.76	2.69	0.01
Pr_4NBr	106.08 ± 0.05	63.71	1.20	0.03
Bu_4NBr	103.60 ± 0.03	13.91	4.68	0.02
		40 W % Dioxane		
Me_4NBr	90.98 ± 0.01	41.16	5.31	0.01
Et_4NBr	86.84 ± 0.02	49.84	5.62	0.02
Pr_4NBr	83.20 ± 0.02	51.08	5.08	0.03
Bu_4NBr	80.76 ± 0.01	27.23	5.60	0.01

Continued...

Table 3–II continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	R_j A°	σ_Λ %
		50 W % Dioxane		
Me_4NBr	79.04 ± 0.01	95.00	6.42	0.01
Et_4NBr	78.13 ± 0.02	115.17	3.76	0.03
Pr_4NBr	73.44 ± 0.01	114.90	5.79	0.01
Bu_4NBr	72.72 ± 0.02	111.98	5.77	0.03
		60 W % Dioxane		
Me_4NBr	69.98 ± 0.01	446.24	6.05	0.01
Et_4NBr	67.66 ± 0.03	267.66	7.42	0.04
Pr_4NBr	63.83 ± 0.07	183.21	9.26	0.09
Bu_4NBr	63.21 ± 0.01	113.67	9.31	0.01
		70 W % Dioxane		
Me_4NBr	57.16 ± 0.01	624.81	10.07	0.05
Et_4NBr	55.69 ± 0.05	703.29	11.48	0.08
Pr_4NBr	55.73 ± 0.04	797.27	8.85	0.06
Bu_4NBr	54.10 ± 0.01	886.77	7.13	0.01
		80 W % Dioxane		
Me_4NBr	39.29 ± 0.01	1375.47	23.18	0.03
Et_4NBr	37.48 ± 0.04	1073.44	28.67	0.09
Pr_4NBr	36.63 ± 0.01	992.53	29.68	0.01
Bu_4NBr	36.95 ± 0.01	786.54	24.27	0.01

Table 3–III: Best–fit parameters for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in dioxane-water mixtures at 25° C, using the FOS conductance equation.

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
		10 W % Dioxane		
Me_4NBr	140.80 ± 0.19	23.52	4.18	0.08
Et_4NBr	139.60 ± 0.11	17.47	4.81	0.04
Pr_4NBr	130.10 ± 0.06	17.94	4.15	0.03
Bu_4NBr	123.60 ± 0.07	8.14	3.38	0.04
		20 W % Dioxane		
Me_4NBr	138.30 ± 0.14	19.79	3.56	0.06
Et_4NBr	136.90 ± 0.17	27.03	3.46	0.10
Pr_4NBr	132.40 ± 0.16	47.64	4.47	0.07
Bu_4NBr	125.10 ± 0.15	30.77	3.90	0.08
		30 W % Dioxane		
Me_4NBr	117.00 ± 0.06	33.19	4.36	0.03
Et_4NBr	111.20 ± 0.04	62.02	5.09	0.02
Pr_4NBr	106.10 ± 0.10	62.51	5.50	0.05
Bu_4NBr	103.50 ± 0.05	11.37	3.53	0.03
		40 W % Dioxane		
Me_4NBr	90.92 ± 0.02	37.26	4.66	0.02
Et_4NBr	86.75 ± 0.04	36.31	4.39	0.04
Pr_4NBr	83.15 ± 0.05	47.76	4.98	0.04
Bu_4NBr	80.70 ± 0.01	22.58	4.24	0.01

Continued...

Table 3–III continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
		50 W % Dioxane		
Me_4NBr	79.02 ± 0.02	88.58	6.16	0.03
Et_4NBr	78.75 ± 0.02	91.17	6.31	0.03
Pr_4NBr	73.41 ± 0.02	109.99	6.69	0.03
Bu_4NBr	72.70 ± 0.03	107.37	6.74	0.04
		60 W % Dioxane		
Me_4NBr	69.95 ± 0.04	438.70	9.85	0.05
Et_4NBr	67.64 ± 0.05	256.64	8.97	0.06
Pr_4NBr	63.79 ± 0.08	165.82	7.54	0.12
Bu_4NBr	63.17 ± 0.01	93.14	6.92	0.01
		70 W % Dioxane		
Me_4NBr	57.12 ± 0.03	591.85	13.09	0.02
Et_4NBr	55.64 ± 0.15	660.49	12.31	0.11
Pr_4NBr	55.71 ± 0.09	772.59	13.94	0.09
Bu_4NBr	54.08 ± 0.03	870.37	14.75	0.02
		80 W % Dioxane		
Me_4NBr	39.16 ± 0.18	947.61	13.75	0.04
Et_4NBr	37.29 ± 0.35	426.50	8.12	0.11
Pr_4NBr	36.44 ± 0.21	322.81	7.32	0.03
Bu_4NBr	36.78 ± 0.09	246.27	10.62	0.01

Table 3–IV: Best–fit parameters for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in dioxane-water mixtures at 25° C, using the Pitts conductance equation.

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
		10 W % Dioxane		
Me_4NBr	140.04 ± 0.12	21.31	2.63	0.12
Et_4NBr	138.61 ± 0.13	14.47	2.69	0.14
Pr_4NBr	129.14 ± 0.13	15.45	2.74	0.15
Bu_4NBr	123.16 ± 0.08	7.30	2.86	0.10
		20 W % Dioxane		
Me_4NBr	137.79 ± 0.09	18.63	2.52	0.10
Et_4NBr	136.48 ± 0.08	26.20	2.50	0.10
Pr_4NBr	131.51 ± 0.14	44.06	2.53	0.14
Bu_4NBr	124.55 ± 0.09	28.68	2.60	0.11
		30 W % Dioxane		
Me_4NBr	116.53 ± 0.07	31.07	2.89	0.07
Et_4NBr	110.56 ± 0.09	57.49	2.83	0.09
Pr_4NBr	105.23 ± 0.13	56.40	2.92	0.16
Bu_4NBr	103.34 ± 0.03	11.41	3.22	0.05
		40 W % Dioxane		
Me_4NBr	90.67 ± 0.04	35.41	3.46	0.09
Et_4NBr	86.55 ± 0.04	36.38	3.41	0.07
Pr_4NBr	82.89 ± 0.05	45.03	3.49	0.08
Bu_4NBr	80.51 ± 0.03	22.18	3.68	0.07

Continued...

Table 3–IV continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
		50 W % Dioxane		
Me_4NBr	78.81 ± 0.04	82.91	4.15	0.11
Et_4NBr	78.54 ± 0.04	84.64	4.17	0.11
Pr_4NBr	73.19 ± 0.04	101.77	4.24	0.11
Bu_4NBr	72.51 ± 0.04	99.65	4.27	0.10
		60 W % Dioxane		
Me_4NBr	69.62 ± 0.07	407.58	5.08	0.13
Et_4NBr	67.41 ± 0.05	236.15	5.33	0.13
Pr_4NBr	63.68 ± 0.05	160.20	5.49	0.13
Bu_4NBr	63.04 ± 0.03	90.53	5.68	0.08
		70 W % Dioxane		
Me_4NBr	56.62 ± 0.35	498.92	7.30	0.70
Et_4NBr	55.23 ± 0.50	584.97	7.17	0.92
Pr_4NBr	55.49 ± 0.40	673.26	7.14	0.88
Bu_4NBr	53.29 ± 0.52	708.31	7.04	1.08
		80 W % Dioxane		
Me_4NBr	39.04 ± 0.03	995.38	11.98	0.04
Et_4NBr	37.40 ± 0.07	607.26	6.05	0.10
Pr_4NBr	36.79 ± 0.01	429.60	4.53	0.02
Bu_4NBr	36.42 ± 0.02	419.36	11.96	0.02

Table 4: Walden Product, $\Lambda_0\eta$, for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in dioxane-water mixture at 25° C.

W %	$\Lambda_0\eta$			
Dioxane	Me_4NBr	Et_4NBr	Pr_4NBr	Bu_4NBr
10	0.9773	0.9681	0.9032	0.8582
20	1.1443	1.1361	1.0972	1.0264
30	1.1346	1.0796	1.0303	1.0038
40	1.0151	0.9695	0.9285	0.9007
50	0.9755	0.9722	0.9062	0.8975
60	0.9009	0.8707	0.8218	0.8132
70	0.9682	0.9450	0.9447	0.9165
80	0.5937	0.5710	0.0561	0.5577

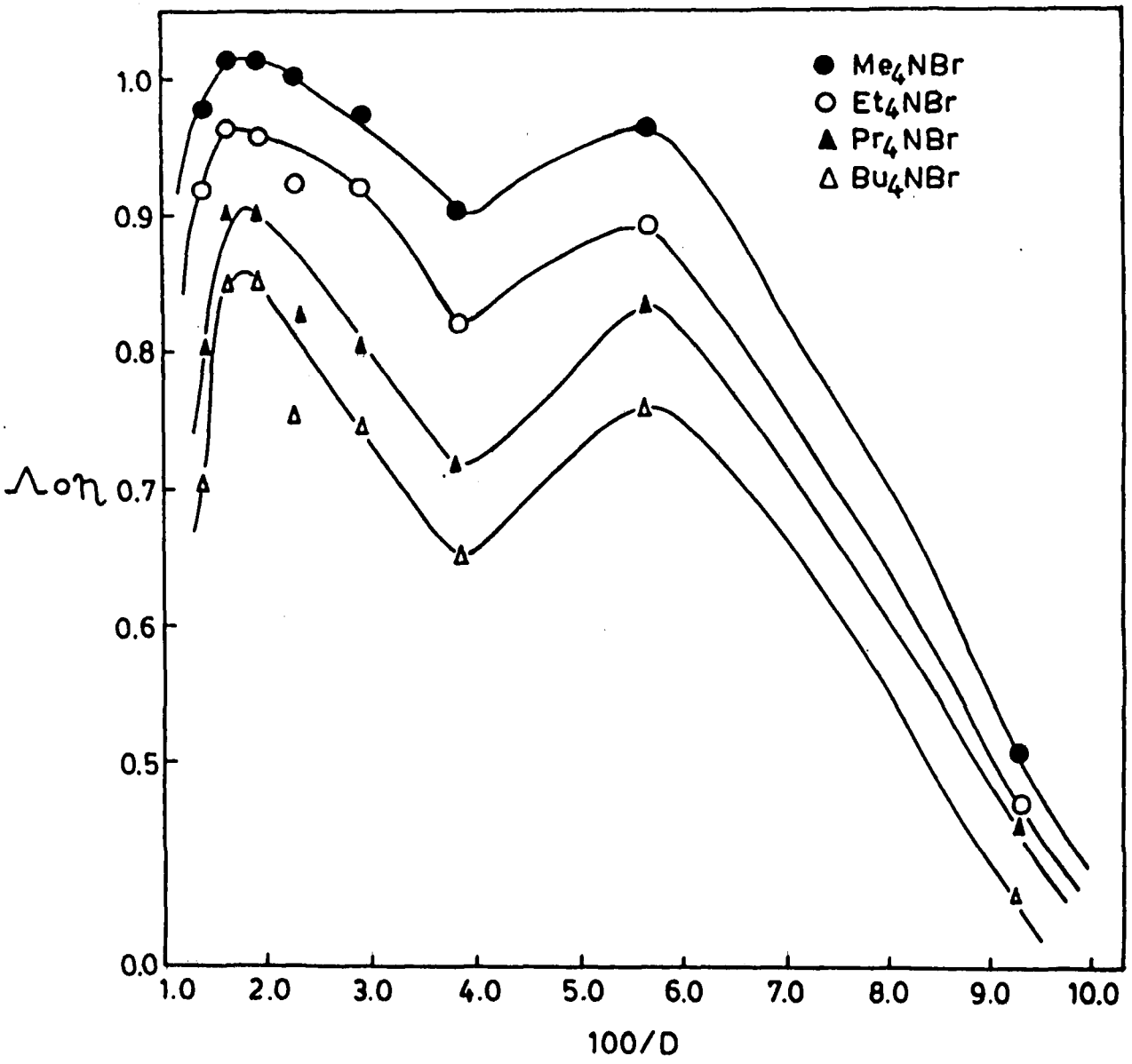

FIG.3. PLOTS OF WALDEN PRODUCTS Vs 1/D FOR Me_4NBr, Et_4NBr, Pr_4NBr AND Bu_4NBr AT 25 °C.

maxima for all the salts under study at D = 60.79 and D = 17.69, which corresponds to 20 W % and 70 W % of dioxane, as have been found in other aqueous binary mixtures for various electrolytes[6, 89, 99 - 102]. It is apparent from Fig. 3 that the Walden product for all the salts passes through a maximum and follows the order, $Me_4NBr > Et_4NBr > Pr_4NBr > Bu_4NBr$. This is due to the increasing size of the cation as discussed earlier and the height of the maximum in the Walden product has been found to be reversed. This type of abnormality has also been observed by other workers[6, 100, 103]. Such a behavior may be explained in the light of the limiting equivalent conductance, the viscosity and the dielectric constant of the medium. It seems that the maxima in the $\Lambda_0\eta$ behavior appear due to the limiting equivalent conductance, Λ_0. The minima in the Walden product are obtained due to the solvent viscosity, because the large tetra-alkyl-ammonium halides[104] ions possess an excess mobility in the solution owing to their ability to break hydrogen bonds in their immediate vicinity and thereby reduce the viscosity of the solvent. Hence, the behavior of $\Lambda_0\eta$ plots may be explained in terms of the ion-solvent interaction.

Although, several attempts have been to explain the variations in the value of Walden product with the composition of mixed solvents in terms of various types of ion-solvent interactions but an overall satisfactory explanation has not yet been offered[6, 55, 99, 101 - 103, 105 - 109]. However, for the present system it can be explained on the

basis of structure breaking and hydrophobic dehydration[99, 101, 102, 105 - 108] of cation due to the presence of co-solvent (dioxane) in the water-rich region. The presence of dioxane molecules may cause hydrophobic dehydration of cations in water-rich region resulting in the excess mobility, which in turns gives rise to a maximum in the Walden product. As the dioxane content increases, the amount of water decreases, so that the hydrophobic dehydration effect will be reduced. On the other hand, ions may be solvated with the other component of the solvent mixture (viz. dioxane). Thus the dehydration will be more effective in the water-rich region producing a maximum while the solvation of ion with dioxane molecules will be more pronounced in the dioxane-rich region resulting in a further decrease in the Walden product after maximum is attained. This explains the variation of Walden product with solvent composition. The presence of maximum in the Walden product may be attributed to the desolvation or dehydration of ions and the height of the maximum may, therefore, depend upon the extent of desolvation or dehydration of ions. Consequently the hydrophobic dehydration effect is more pronounced in the case of an ion which is more hydrophobic in nature and varies in order[55, 109] $Bu_4N^+ > Pr_4N^+ > Et_4N^+ > Me_4N^+$. The height of the maximum in the Walden product is expected to follow the order $Bu_4N^+ > Pr_4N^+ > Et_4N^+ > Me_4N^+$, while in the present case the order is $Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$, seemingly due to an increase in the size and the hydrophobic solvation of cations in the same order,

causing a decrease in the mobility of ions. This behavior is in accord with the results reported earlier[6, 99, 101 - 103, 105].

Association Constant

The association constants, K_A obtained from several conductance equations are presented in Table 3 (I-IV). The K_A values obtained from F78 equation (Table 3-I) are always greater than those obtained from the J (Table 3-II), FOS (Table 3-III) and P (Table 3-IV) equations and follow the order F78 > J > FOS > P. The values of the average percent difference between the association constants calculated through the F78 equation are 14.79 %, 25.06 % and 29.45 % higher than those obtained from J, FOS and P equations, respectively. This uncertainty seems to stem purely from the ambiguities in the theories and consequently, it is not appropriate at the moment to suggest the relative superiority of one equation over that of the other. An examination of Table 3 shows that the ionic association is least in the case of 10 W % dioxane while it is highest in that of 80 W % dioxane. The overall values of association constant increase with a decrease in the solvent dielectric constant of the medium. The non-linear plots of log K_A versus 1 / D (Fig. 4) shows that the K_A values obtained from F78, J, P and FOS equations are in contrast to the expected behavior in the light of the Justice-Bjerrum theory[43, 110].

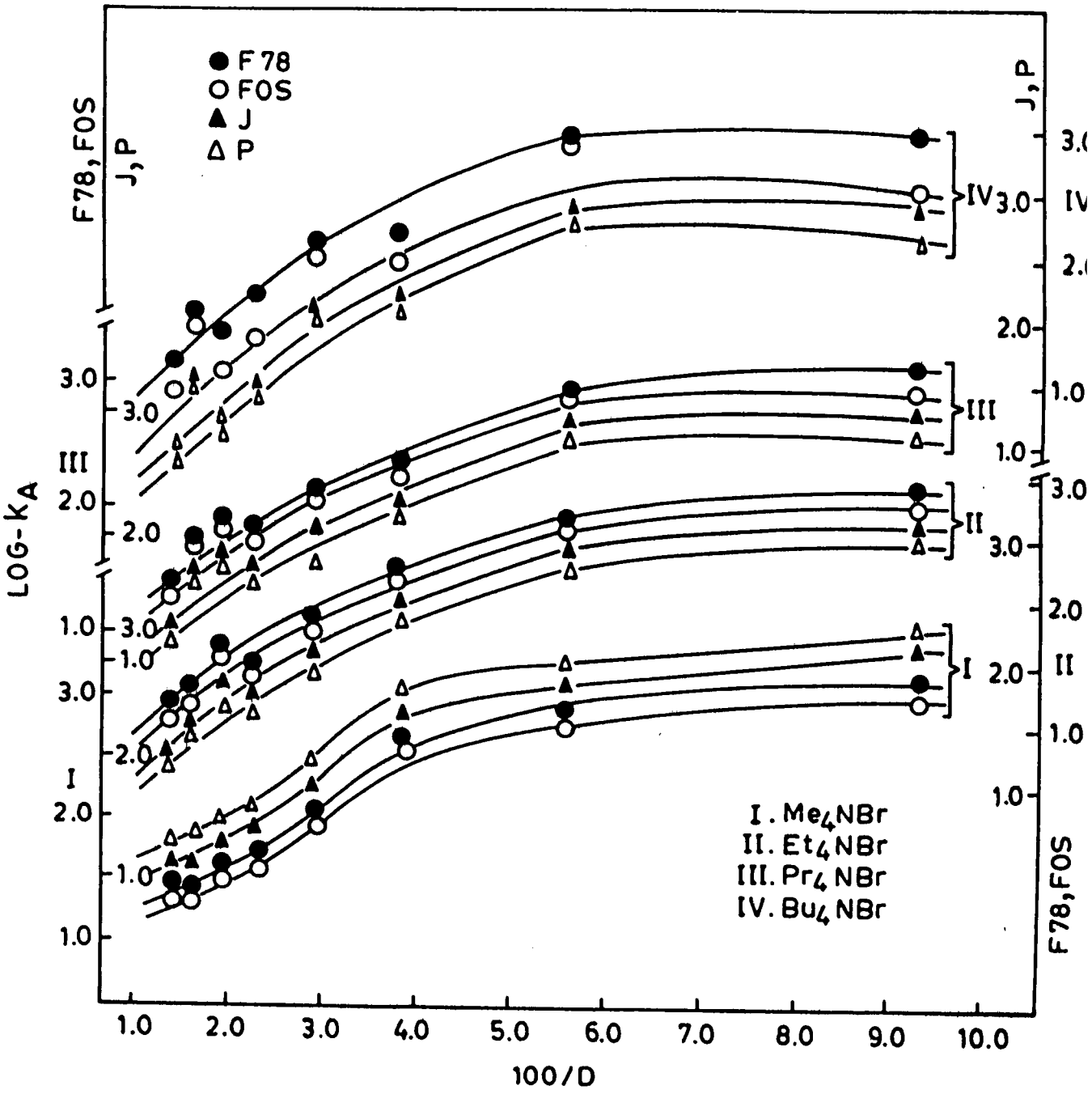

FIG. 4. PLOTS OF LOG K_A Vs 1/D.

An inspection of Table 3 further reveals that the K_A values for Me_4NBr, Et_4NBr and Pr_4NBr in a given dielectric constant increase with the increasing size of the cations and follow the order $Me_4N^+ < Et_4N^+ < Pr_4N^+$ in the dielectric range ($60.79 \leq D \leq 42.98$) but the order is found to be $Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+$ in the case of 50 and 70 W % dioxane mixtures as expected[99-102], in view of the hydrophobic solvation of ions being increased with the increasing proportion of dioxane in the same order. However, this order does not carry-over in the case of 60 and 80 W % dioxane and follows the order $Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$ as reported earlier[41, 81, 111, 112]. Such an anomalous behavior of K_A values in the low dielectric medium may be ascribed to the predominant solvation of cations[113] due to increasing charge density with decrease in the size, which apparently controls the extent of ion pairing in the dioxane-rich region. Thus, the association of large ions in hydrogen-bonded solvent is expected to be hindered by their inability to solvate, which further decreases with increase in the size of cations. This effect appears to be governed by the degree of solvation of cations as well as the protic properties of the solvent[114, 115]. Consequently, it may be noted that the resultant association appears to depend upon two opposing behavior of ions, viz., first (I) an increase in the solvation with increasing ionic size and the consequent increase in the K_A values due to the formation of the solvent separated ion-pairs (SSIP) and second (II) a decrease in

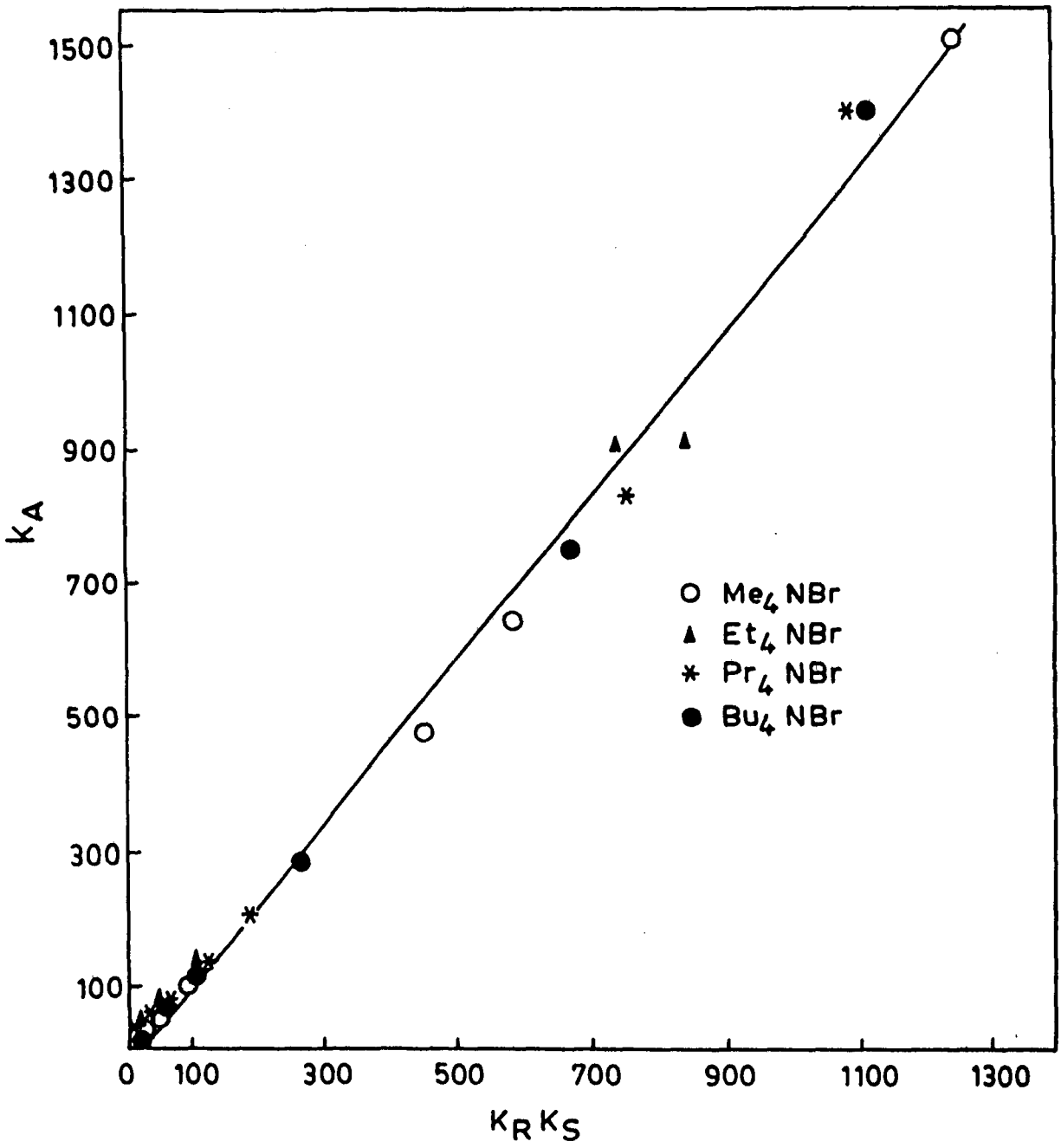

FIG. 5. DEPENDENCE OF IONIC-ASSOCIATION, K_A ON THE PRODUCT $K_R K_S$.

solvation with increasing ionic-size leading to an increase in the K_A values due to the formation of contact ion-pairs (CIP). This may be represented by the two-step equilibria[16, 17, 19, 95],

$$R_4N^+(S)_m + X^-(S)_n \rightleftharpoons \underset{\text{(SSIP)}}{R_4N^+SSX^-} \text{ or } R_4N^+SX^-\,S \text{ or } SR_4N^+SX^- + S\ (m+n-2) \quad (1.14)$$

$$\Updownarrow$$

$$\underset{\text{(CIP)}}{SR_4N^+X^-\,S} \text{ or } R_4N^+\,X^-\,SR_4N^+X^-\,S$$

where S denotes the solvent molecules while m and n are the solvation numbers of the ions. In view of the above discussion, the association behavior may be expressed in terms of K_R and K_S whose variation resemble those of the K_A values,

$$K_A = K_R\,(1 + K_S) \quad (1.15)$$

in which K_R and K_S denote the SSIP and CIP formation constants, respectively. The linear plot of K_A versus the product of K_RK_S (Fig. 5) support the applicability of the above equation.

Hence, the F78 method of analysis helps in evaluating the values of K_R and K_S (Table 3-I). As apparent from the table the overall values of K_R increase with a decrease in the dielectric constant

of the medium, while K_S values seem to be independent of the dielectric constant and the size of the cations. Consequently, the overall association constant is greater in 10 %, 20 %, 30 %, 40 %, 50 % and W 70 % dioxane-water mixtures for the larger size of the cations than those for the smaller ions. This seems to be due to the formation of SSIP. However, in the cases of 60 % and 80 W % the association constant is found to be greater for smaller ions than those for the larger ones. Therefore, tetra-alkyl-ammonium bromides appear to form a contact ion-pair (CIP) in 60 and 80 W % dioxane-water mixtures.

Distance and Ion-size Parameters

The values of the distance or ion-size parameters (R or a°) obtained from different equations based on the theories of ion-association employed to predict the K_A values, are compared with those of the crystallographic radii of the salts under study. The distance parameter or Gurney cosphere diameter, R (Table 3 – I) obtained from F78 equation for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr are found to be larger than those of the distance of closest approach, R_j (Table 3 – II) and the ion-size parameter, $a_k°$ (Table 3 – III and IV) obtained from the J, P and FOS equations. These values in the cases of 10, 20 and 30 W % dioxane solutions obtained from the J, and in those of 10, 20, 30 and 40 W % dioxane solutions from P, and similarly in

those of 10, 20, 30 and 40 W % dioxane solutions (only for Bu_4NBr) from FOS equations are smaller than the crystallographic radii of the ion-pair showing average deviations in the values of R or $a_k°$ to be ~ –3.55, ~ –5.55 and ~ –3.26 (from J. P and FOS equations) respectively. However, the R values computed through the F78 equation are reasonable and higher than the Bjerrum distance, q, whereas $R_j \leq q$. Similarly, in the case of $a_k°$ values obtained from the FOS equation $a_k° \leq q$ while a° obtained from the P equation is less than q. Consequently, it is apparent from Table 3 that the values of R or a° do not show any significant variation with the size of the cations but they increase with decrease in the dielectric constant of the medium which, in turn supports an increase in the ionic association.

CHAPTER II

STUDIES OF ELECTRICAL CODUCTIVITY AND IONIC-ASSOCIATION OF TETRA-ALKYL AMMONIUM - HALIDES IN ETHYLENE GLYCOL WATER MIXTURES AT 25°C

RESULTS AND DISCUSSION

Electrical Conductance

The molar conductivities, Λ (S cm^2 mol^{-1}) of dilute solutions of Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in ethylene glycol-water (EG–H_2O) mixtures of different dielectric constant values covering the range $37.7 \leq D \leq 75.6$ have been measured as a function of concentration C (mol. dm^{-3}) at 25° C (Table 5).

The conductance data of the above solutions have been analyzed by using F78, FOS, J and P conductance equations for associated as well as unassociated electrolytes as done in the case of dioxane-water (cf. Chapter I) mixtures. The initial values of the limiting equivalent conductance, Λ_0, used in the analysis of the above conductance equations were obtained from Shedlovsky's[28] method of extrapolation of conductance data as done earlier (Chapter I) by using the expression,

$$\Lambda_0' = \frac{\Lambda_{obs} + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} \qquad (2.1)$$

$$= \Lambda_0 + BC \qquad (2.2)$$

Table 5: Molar conductivities, Λ (S cm^2 mol^{-1}) and molar concentration C (mol dm^{-3}) of Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in Ethylene glycol water mixture at 25° C.

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			10 W % Ethylene glycol				
847.00	81.587	757.73	73.490	475.37	69.239	543.56	65.495
770.00	82.701	658.84	74.968	377.61	71.494	459.38	67.196
651.00	84.063	582.56	76.229	332.29	72.864	385.75	68.906
564.00	85.175	473.33	78.257	267.98	74.659	314.96	70.790
483.00	86.260	302.93	82.334	224.52	76.118	265.74	72.282
338.80	88.430	233.02	84.449	184.60	77.643	217.42	73.934
		189.33	85.986	151.04	79.150		
				127.80	80.219		

Continued...

Table 5 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			20 W % Ethylene glycol				
607.77	69.390	638.96	60.681	555.70	55.407	681.68	47.843
494.24	71.308	524.86	62.759	459.89	57.140	568.06	49.409
339.39	73.345	419.88	64.881	370.45	59.080	470.12	51.265
332.83	74.797	341.77	66.660	317.54	60.375	389.53	52.927
268.18	76.610	277.27	68.484	256.47	61.992	332.52	54.186
225.46	77.814	233.27	69.954	208.38	63.444	278.23	55.628
183.93	79.275	193.36	71.408	175.48	64.533	231.07	57.023
155.32	80.385	163.29	72.540	148.18	65.532	194.76	58.225
82.22	83.525			78.45	68.415		

Continued...

Table 5 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			30 W % Ethylene glycol				
640.01	57.332	510.88	50.544	592.63	44.111	643.21	40.720
533.34	58.636	422.79	52.146	493.85	45.452	536.07	42.195
441.38	59.965	350.31	53.665	395.08	47.218	428.81	44.017
355.56	61.403	291.93	54.983	329.23	48.470	338.53	45.642
237.04	63.792	235.79	56.579	257.66	50.129	268.00	47.264
188.23	65.163	188.63	58.124	204.35	51.570	214.40	48.564
152.38	66.225	153.26	59.448	164.61	52.826	135.41	50.953
128.00	67.119	126.40	60.633	134.68	53.771	91.18	52.942
		60.10	64.127			76.57	53.718

Continued...

Table 5 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			40 W % Ethylene glycol				
460.85	47.899	554.81	41.108	494.98	34.198	559.27	28.802
368.68	49.510	443.85	42.793	395.98	35.960	466.06	30.162
291.06	51.076	382.63	43.837	309.36	37.769	372.85	31.820
225.72	52.606	308.23	45.393	219.99	40.368	279.63	34.074
176.34	54.018	236.01	47.154	164.99	42.294	203.37	36.389
188.86	55.281	184.93	48.621	126.91	43.926	98.69	40.956
113.36	56.296	146.00	49.995	101.01	45.417	56.39	43.779
81.32	57.711	116.80	51.179	58.23	48.163	35.88	45.477
65.06	58.493			48.52	48.959		
54.21	59.105			37.67	49.928		

Continued...

Table 5 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			50 W % Ethylene glycol				
485.55	38.571	348.58	34.424	486.16	28.653	473.50	25.958
346.10	40.029	252.72	36.579	347.25	30.818	326.55	28.576
173.05	43.394	183.79	40.755	216.07	33.764	210.44	31.572
121.13	44.687	123.27	41.755	138.90	36.416	135.28	34.226
61.07	46.770	63.71	43.843	68.74	39.716	96.70	36.227
43.85	47.500	42.74	45.354	45.83	41.269	30.00	40.982
				29.46	42.628		

Continued...

Table 5 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			60 W % Ethylene glycol				
416.80	29.176	405.90	30.652	403.80	29.975	406.70	28.960
257.50	32.425	320.60	32.114	307.95	31.765	312.26	30.730
205.68	33.882	251.64	33.580	235.60	33.530	250.62	32.210
176.25	34.875	198.65	34.960	186.84	35.020	204.75	33.540
125.32	36.966	155.64	36.316	145.79	36.565	175.62	34.545
96.72	38.440	106.48	38.273	129.72	37.260	154.67	35.350
78.52	39.550	84.15	39.366	88.42	39.440	137.35	36.110
68.54	40.240	70.52	40.125	71.84	40.510	106.82	37.620
50.74	41.260	55.62	40.998	57.42	41.620	88.65	38.685
37.85	42.780	47.75	41.610	48.62	42.330	72.15	39.814
27.89	43.835	35.86	42.520	40.35	43.110	59.35	40.810
23.57	44.240			30.29	44.126	45.78	41.990
						40.62	42.510

Continued...

Table 5 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			70 W % Ethylene glycol				
351.00	28.730	338.90	27.640	328.50	26.510	293.13	26.095
282.61	30.136	265.20	29.130	247.80	28.285	227.20	27.790
227.95	31.530	206.75	30.635	198.85	29.660	185.32	29.092
186.82	32.768	175.32	31.615	159.75	31.013	146.70	30.545
167.42	33.470	146.52	32.650	135.26	32.025	125.60	31.500
148.92	34.185	128.95	33.376	119.87	32.750	109.87	32.310
128.67	35.086	107.65	34.370	97.34	33.950	88.65	33.585
102.31	36.388	88.25	35.425	82.64	34.865	78.64	34.244
87.82	37.241	72.35	36.415	69.72	35.775	65.71	35.215
71.65	38.201	63.72	37.020	59.81	36.556	55.84	36.050
65.32	38.774	55.64	37.630	49.65	37.465	48.62	36.730
53.86	39.690	48.92	38.172	44.75	37.940	40.96	37.536
48.85	40.125					35.72	38.115
						32.64	38.490

Continued...

Table 5 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			80 W % Ethylene glycol				
200.70	25.780	225.80	24.490	220.37	22.770	198.16	23.066
155.29	27.450	201.40	25.192	155.62	24.884	146.75	24.900
127.23	28.690	165.24	26.392	130.15	25.986	125.42	25.870
102.50	29.980	137.42	27.515	109.87	27.010	106.25	26.900
93.52	30.530	115.24	28.570	97.23	27.750	95.82	27.540
82.34	31.250	107.52	28.980	87.54	28.380	87.84	28.065
74.52	31.850	95.24	29.695	77.85	29.080	79.54	28.670
65.74	32.560	88.62	30.116	69.52	29.715	70.23	29.420
56.32	33.400	79.62	30.734	60.78	30.520	63.85	29.992
43.52	34.730	70.54	31.410	54.68	31.110	57.84	30.560
36.54	35.570	64.51	31.900	48.92	31.730	50.26	31.300
30.45	36.392	57.92	32.486			45.51	31.920

Continued...

Table 5 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			90 W % Ethylene glycol				
180.90	22.485	163.40	23.260	132.34	21.804	151.28	21.028
157.42	23.206	135.26	24.358	115.26	22.507	127.35	21.951
127.60	24.284	114.83	25.198	100.78	23.239	108.75	22.801
108.53	25.126	100.65	25.882	91.67	23.732	98.42	23.332
97.64	25.644	91.23	26.368	82.58	24.283	89.54	23.842
86.73	26.235	82.54	26.867	74.69	24.778	79.84	24.460
78.59	26.720	71.38	27.592	65.32	25.467	70.85	25.088
70.65	27.210	63.43	28.148	59.43	25.938	64.79	25.550
64.82	27.624	55.82	28.747	54.65	26.350	59.72	25.976
58.24	28.120	49.76	29.278	49.82	26.798	53.87	26.495
50.34	28.780	42.37	29.996	44.53	27.330	48.69	27.010
44.62	29.310	39.86	30.260	40.21	27.802	46.56	27.768

Continued...

Table 5 continued

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ	C x 10^4	Λ
			100 % Ethylene glycol				
113.90	20.658	85.03	20.296	92.83	17.025	89.33	16.685
100.68	21.226	78.64	20.670	81.56	17.557	79.42	17.180
92.31	21.710	58.43	21.330	73.24	18.010	69.85	17.724
83.54	22.211	61.54	21.685	67.51	18.340	59.74	18.328
73.78	22.830	57.42	22.156	60.25	18.816	54.37	18.770
66.72	23.320	52.54	22.580	55.84	19.124	48.06	19.220
59.46	23.884	48.67	22.930	50.79	19.515	42.58	19.788
49.85	24.735	42.73	23.526	46.15	19.910	37.56	20.290
40.67	25.688	36.85	24.110	41.53	20.322	31.54	20.992
34.85	26.380	30.29	24.660	36.89	20.780	27.94	21.455
29.87	27.066	27.54	25.422	30.75	21.478	22.87	22.195
25.87	27.670	23.85	26.010	27.54	21.877	20.74	22.550
23.67	28.044	20.95	26.512	24.68	22.280	17.56	23.130
		17.85	27.120	20.87	22.855	15.49	23.535

where α and β have their usual significance. The values of Λ_0 thus calculated by using equation (2.1) are least squares fitted to equation (2.2). The plots of Λ_o' versus C (Figs 6.1 to 6.10) for all the salts are found to be linear. The Λ_0 values thus obtained were used as initial values in the analysis of conductance data by F78, J, P and FOS equations.

The computed values of the adjustable parameters, Λ_0, K_A, K_R, K_S and R of F78 and Λ_0, K_A, R_j or a° of FOS, J and P equations along with the minimum standard deviation, σ_Λ % (i.e. σ_{min} x 100 / Λ_0) are listed in Table (6 – I to 6 – IV), respectively.

Limiting Equivalent Conductance

The values of Λ_0, obtained for all the salts from F78 and J equations are found to be almost close to each other with an average deviation of ~ ± 0.082 % and ~ ± 0.063 %, respectively, while those obtained from the FOS and P equations are ~ ± 0.1 % and ~ ± 0.155 %, respectively. An inspection of Table 6(I – IV) reveals that the Λ_0 value decreases in various solvent mixtures of decreasing dielectric constant value and also with increase in the size of the cations in the order, $Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$. It is noteworthy that in the dielectric range $63.20 \geq D \geq 37.70$, the extent of decrease in the Λ_0 values with increasing cationic size is insignificant while in the range

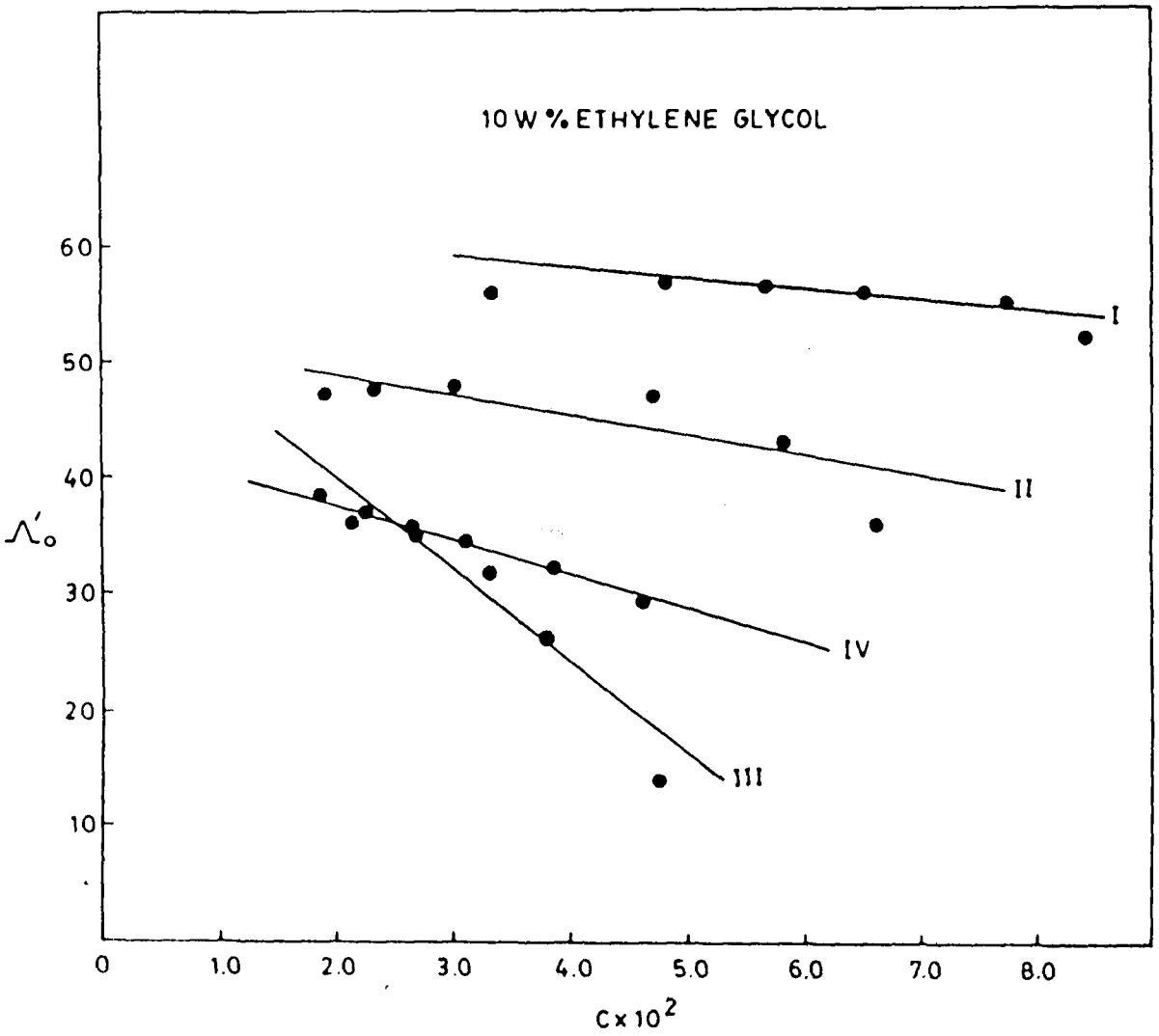

FIG. 6.1. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL-WATER MIXTURES AT 25 °C.

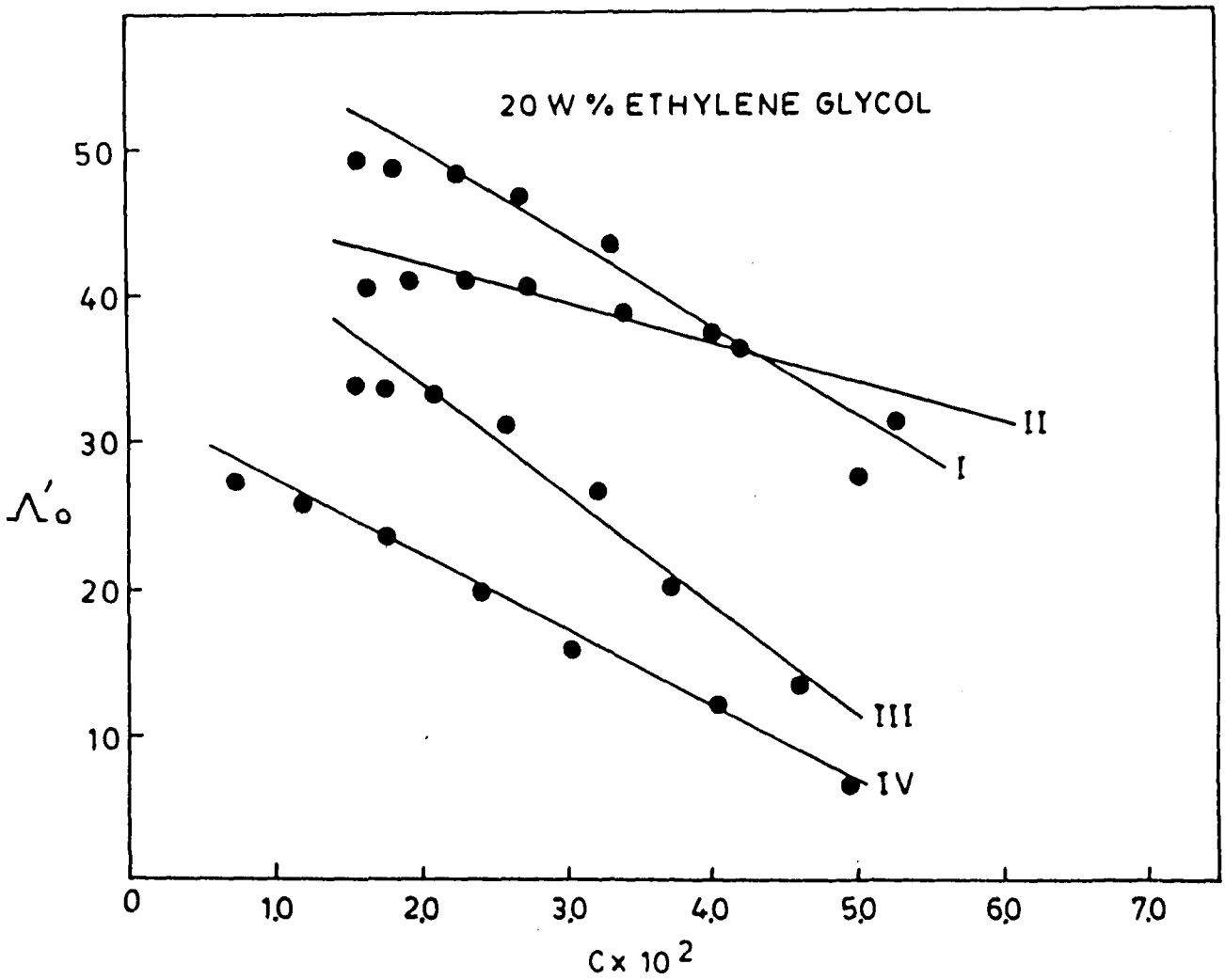

FIG. 6.2. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL - WATER MIXTURES AT 25°C.

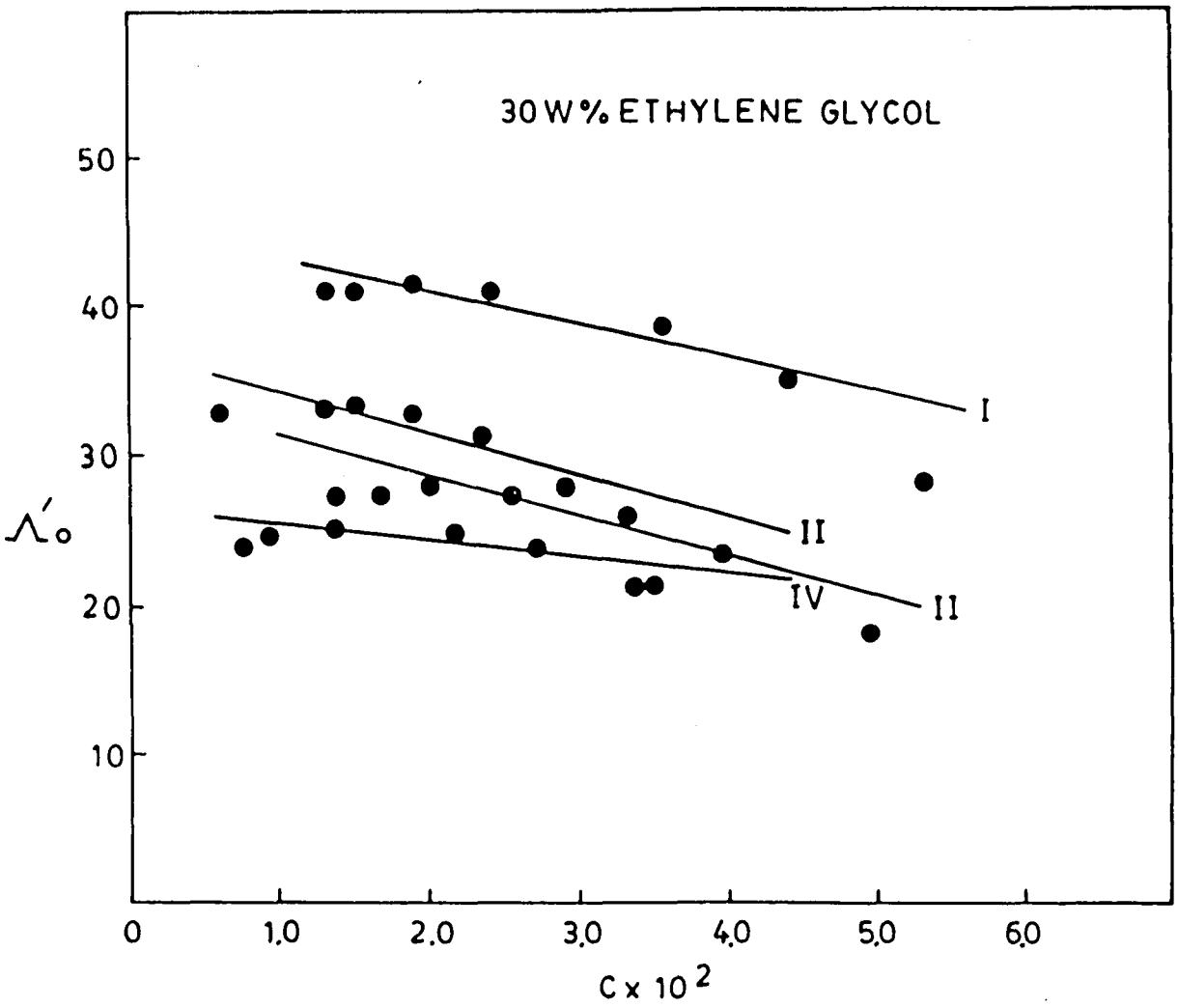

FIG. 6.3. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL-WATER MIXTURES AT 25 °C.

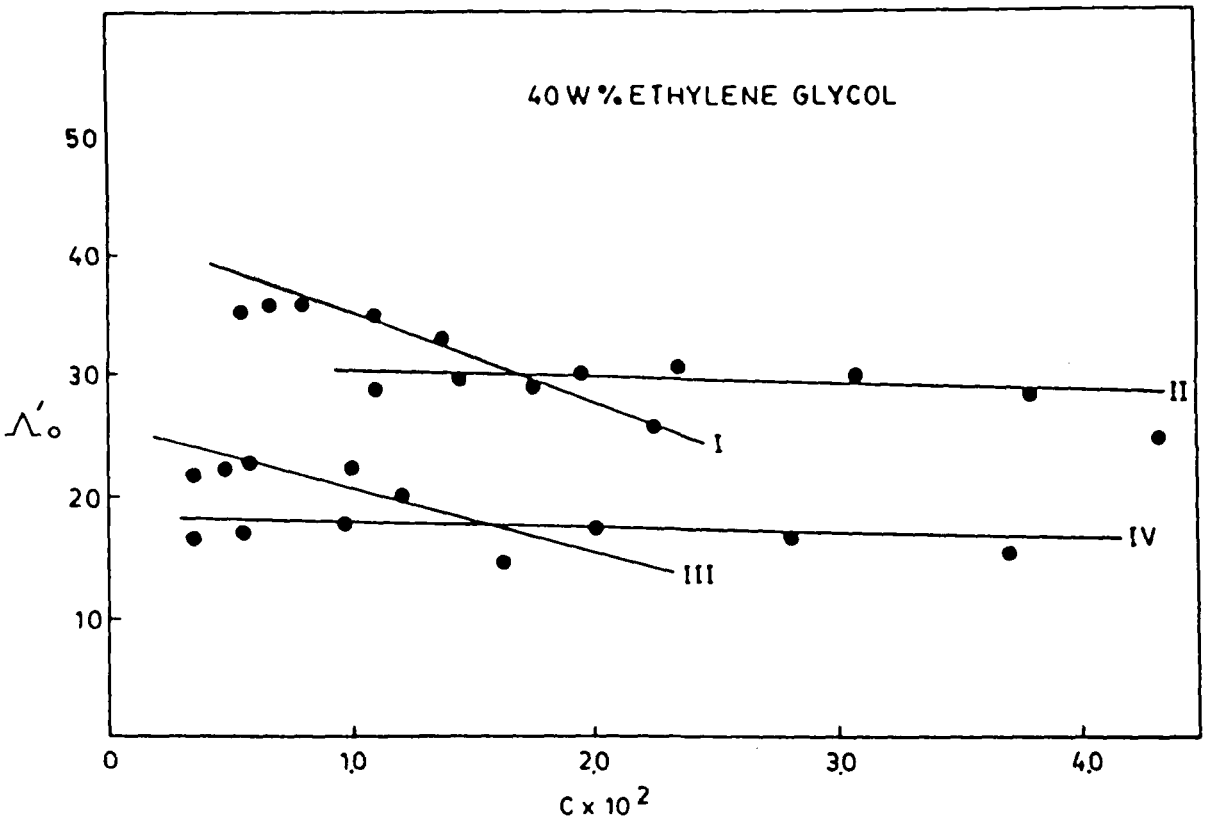

FIG. 6.4. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL-WATER MIXTURES AT 25°C.

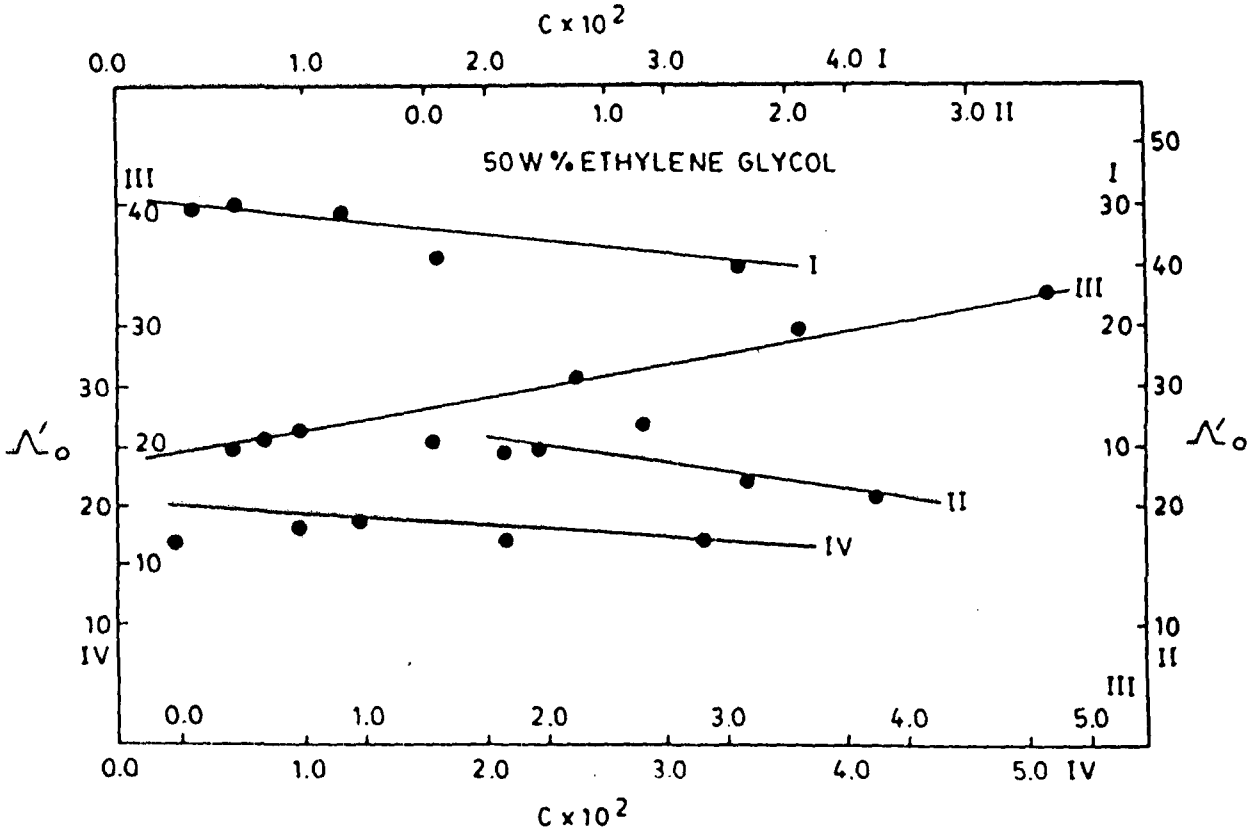

FIG.6.5. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL - WATER MIXTURES AT 25°C.

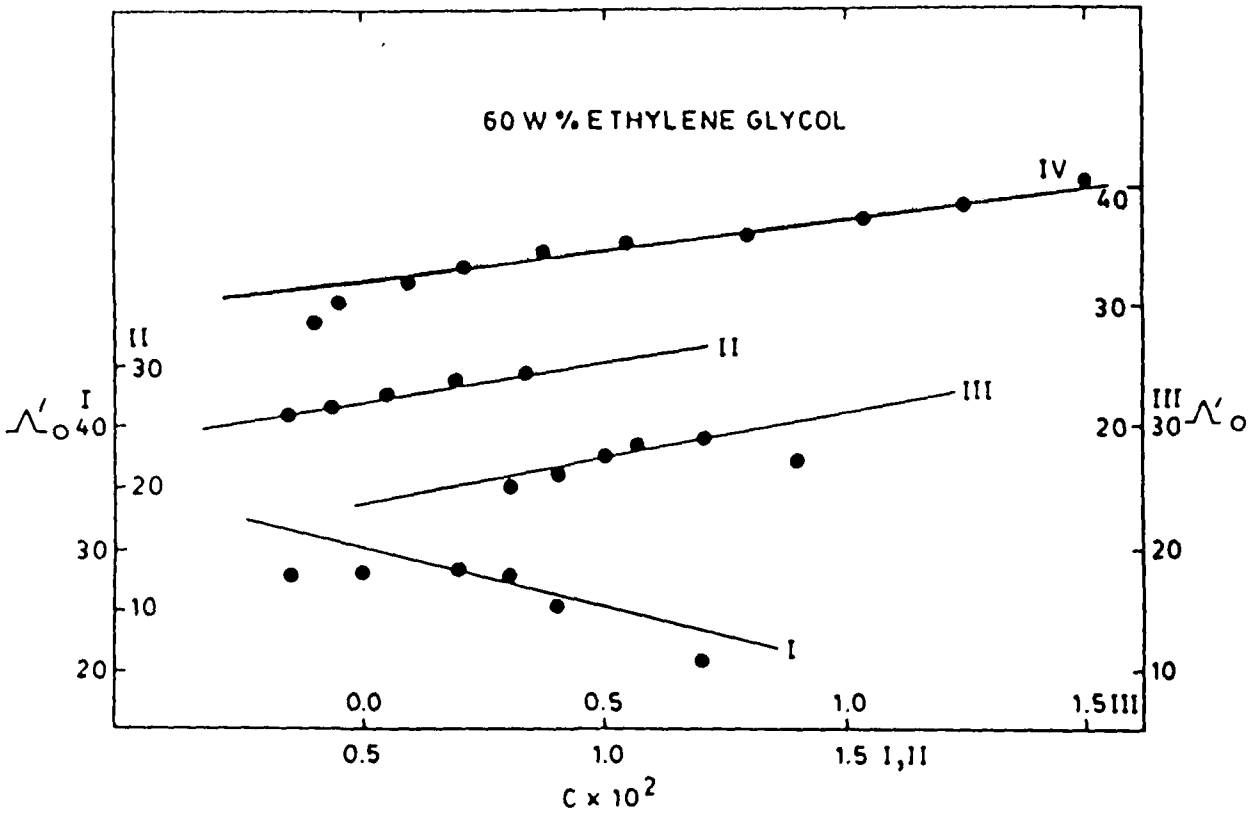

FIG.6.6. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL - WATER MIXTURES AT 25 °C.

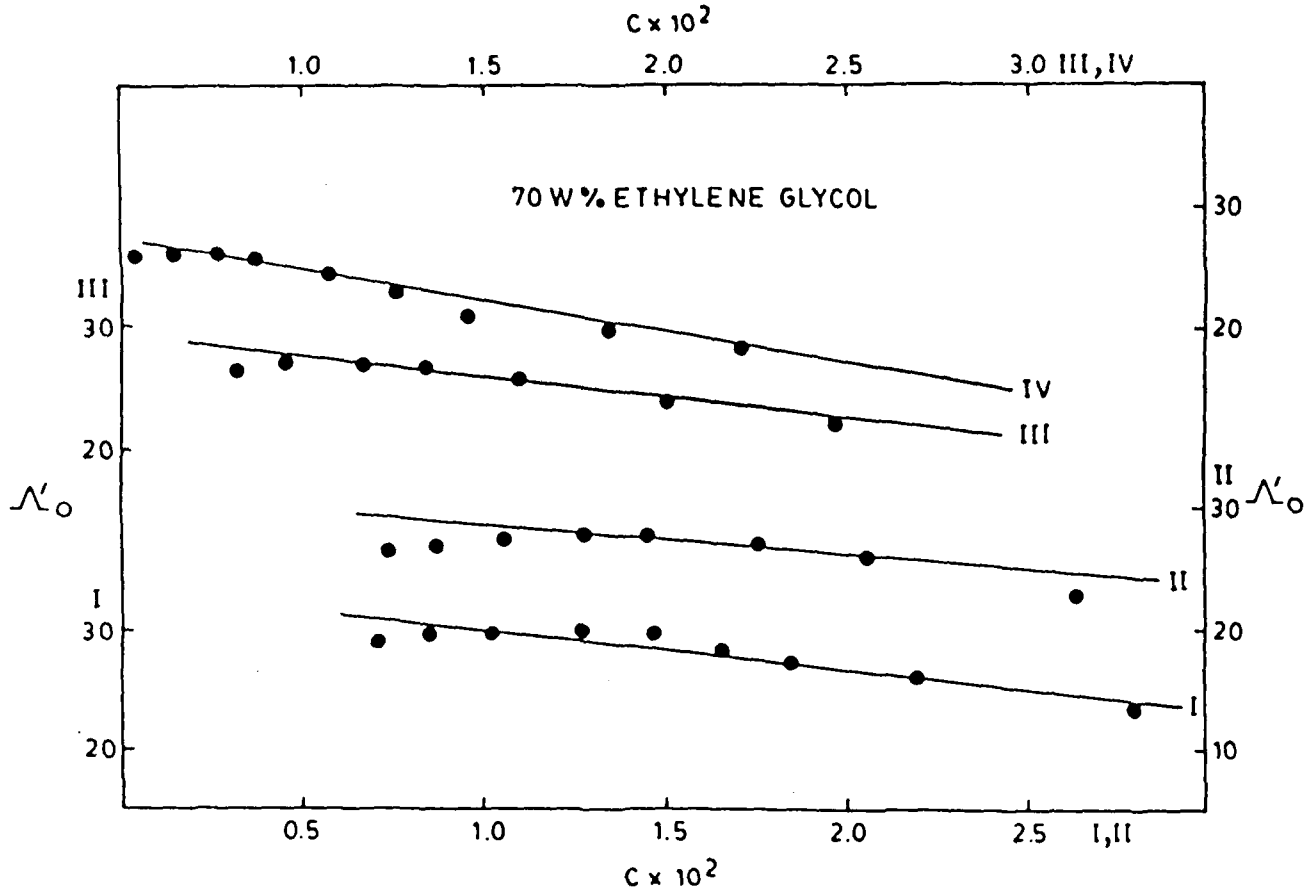

FIG.6.7. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL - WATER MIXTURES AT 25 °C.

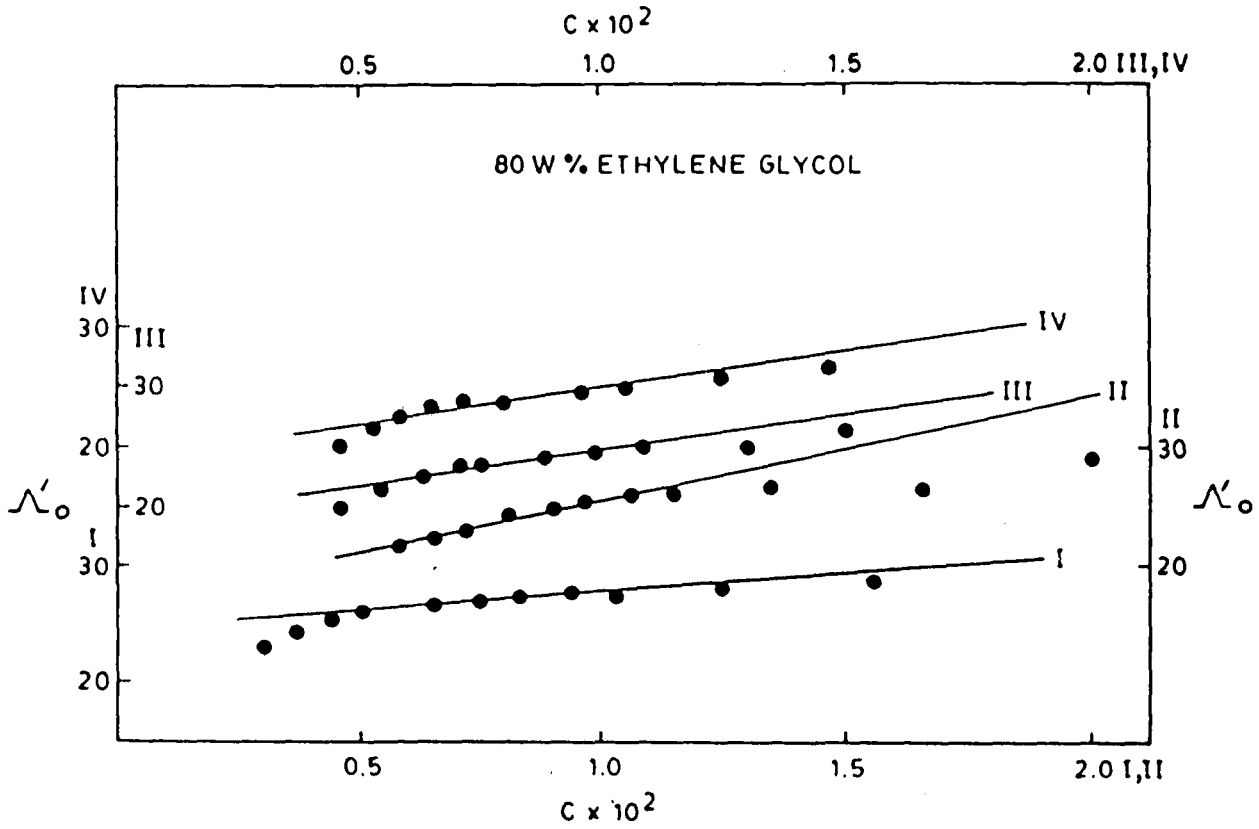

FIG.6.8. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL-WATER MIXTURES AT 25 °C.

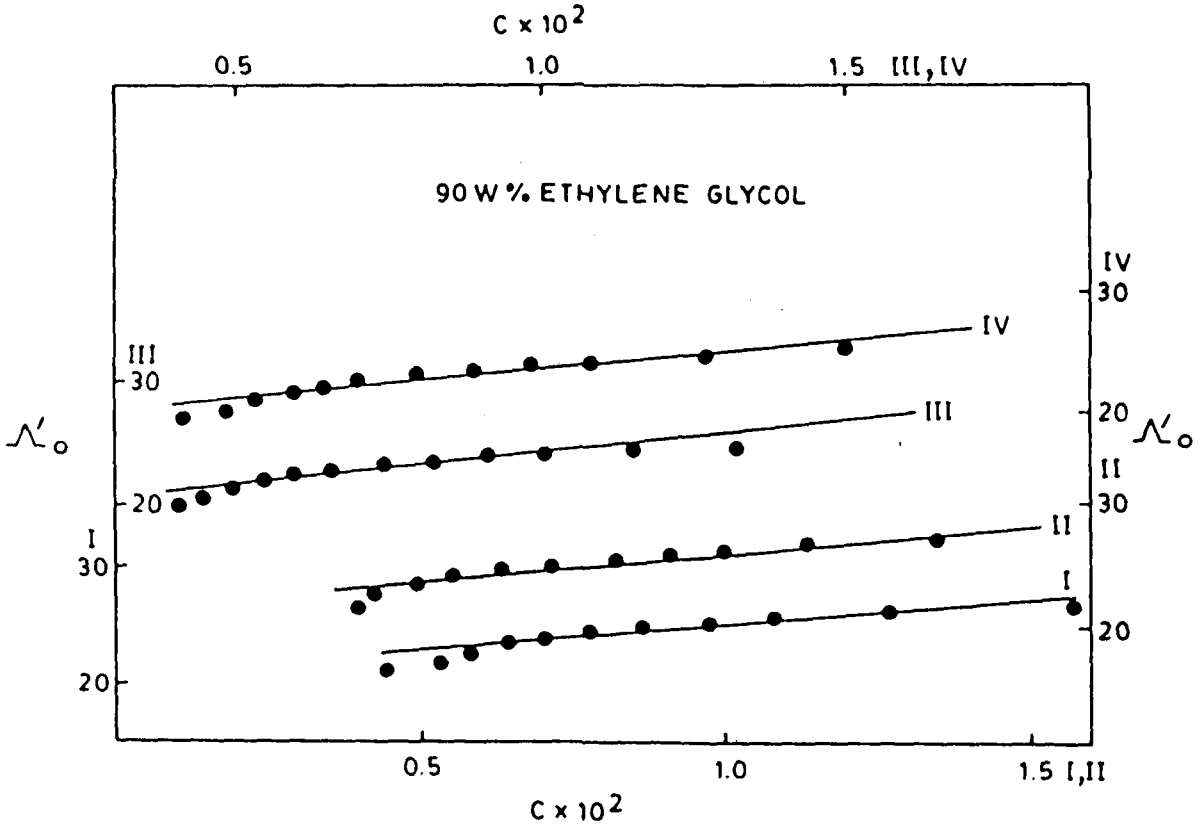

FIG.6.9. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL - WATER MIXTURES AT 25 °C.

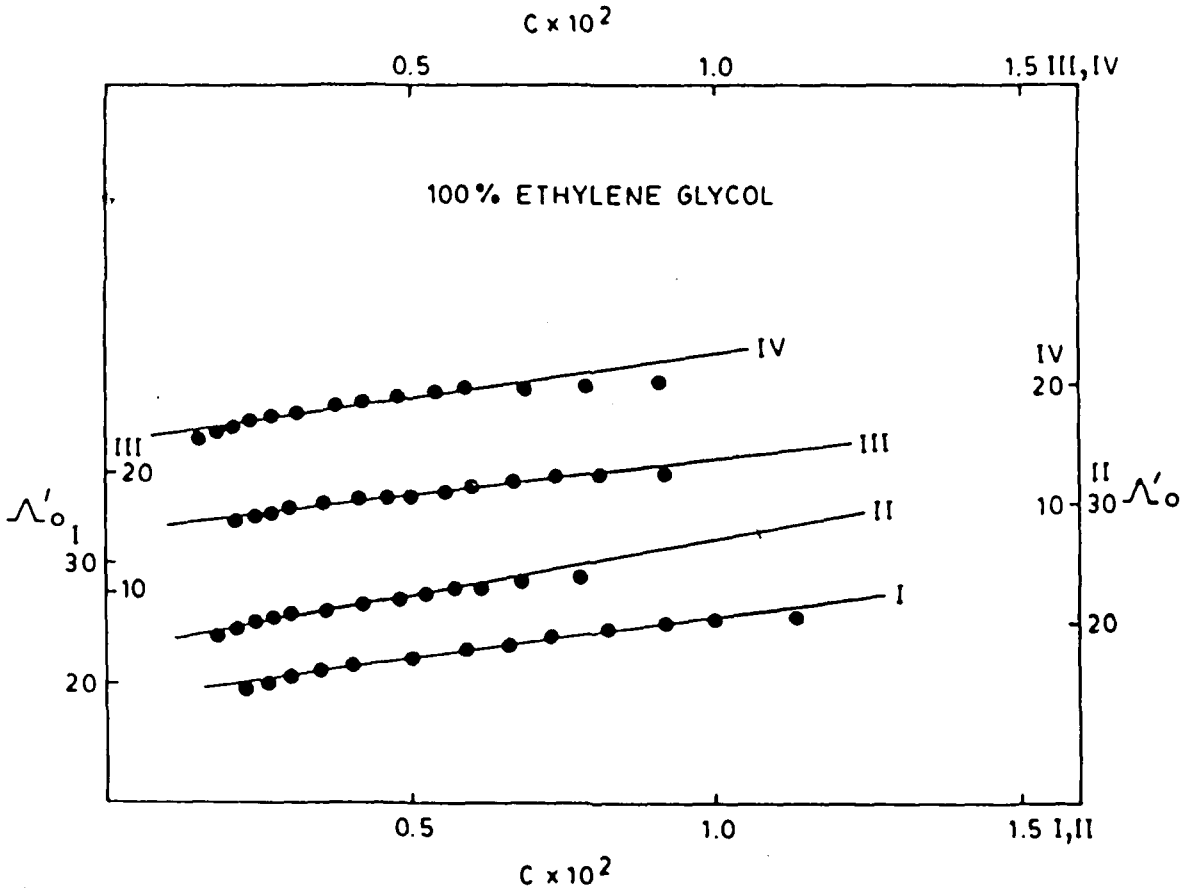

FIG.6.10. PLOTS OF Λ'_o Vs C FOR Me_4NBr (I), Et_4NBr (II), Pr_4NBr (III) AND Bu_4NBr (IV) IN ETHYLENE GLYCOL - WATER MIXTURES AT 25 °C.

Table 6–I: Best–fit parameters for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in ethylene glycol–water mixtures at 25° C, using the F78 conductance equation.

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	K_R	K_S	R A°	α Alpha	σ_Λ %
			10 W % Ethylene glycol				
Me_4NBr	102.48 ± 0.24	4.60	1.69	1.72	5.65	0.6327	0.09
Et_4NBr	99.75 ± 0.02	7.96	1.77	3.48	5.82	0.7769	0.01
Pr_4NBr	92.08 ± 0.10	9.54	1.58	5.01	5.44	0.8337	0.06
Bu_4NBr	89.70 ± 0.02	10.16	1.69	5.01	5.64	0.8337	0.01
			20 W % Ethylene glycol				
Me_4NBr	91.71 ± 0.10	8.31	1.65	4.02	5.40	0.8011	0.09
Et_4NBr	85.46 ± 0.09	11.01	1.75	5.29	5.60	0.8410	0.06
Pr_4NBr	76.46 ± 0.29	10.78	1.85	4.81	5.80	0.8279	0.24
Bu_4NBr	72.21 ± 0.16	14.17	2.08	5.81	6.20	0.8532	0.09
			30 W % Ethylene glycol				
Me_4NBr	75.49 ± 0.07	7.24	1.40	4.14	4.60	0.8085	0.07
Et_4NBr	70.87 ± 0.03	12.73	1.75	6.24	5.40	0.8621	0.04
Pr_4NBr	63.53 ± 0.11	12.56	1.85	5.76	5.60	0.8521	0.10
Bu_4NBr	60.79 ± 0.14	13.52	1.93	5.98	5.75	0.8568	0.21

Continued...

Table 6 – I continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	K_R	K_S	R A°	α Alpha	σ_Λ %
		40 W % Ethylene glycol					
Me_4NBr	64.51 ± 0.02	12.14	1.93	5.26	5.50	0.8403	0.04
Et_4NBr	60.25 ± 0.03	15.28	1.88	7.10	5.40	0.8765	0.03
Pr_4NBr	55.69 ± 0.04	25.96	2.33	10.11	6.20	0.9100	0.08
Bu_4NBr	51.82 ± 0.24	37.71	4.90	6.60	9.20	0.8700	0.39
		50 W % Ethylene glycol					
Me_4NBr	51.10 ± 0.10	10.99	1.91	4.74	5.12	0.8260	0.21
Et_4NBr	50.68 ± 0.03	25.10	2.71	8.26	6.50	0.8920	0.05
Pr_4NBr	46.93 ± 0.06	28.39	2.67	9.60	6.45	0.9057	0.12
Bu_4NBr	46.23 ± 0.30	38.81	3.38	10.45	7.40	0.9127	0.43
		60 W % Ethylene glycol					
Me_4NBr	47.03 ± 0.01	30.02	3.49	7.60	7.20	0.8837	0.04
Et_4NBr	48.51 ± 0.01	38.48	3.29	10.69	6.95	0.9145	0.01
Pr_4NBr	49.20 ± 0.01	42.68	5.71	6.46	9.40	0.8661	0.02
Bu_4NBr	49.01 ± 0.01	46.35	5.59	7.28	9.30	0.8793	0.01

Continued...

Table 6 – I continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	K_R	K_S	R A°	α Alpha	σ_Λ %
		70 W % Ethylene glycol					
Me_4NBr	47.33 ± 0.03	47.03	4.85	8.69	8.20	0.8968	0.06
Et_4NBr	45.10 ± 0.01	48.99	6.04	7.10	9.25	0.8766	0.01
Pr_4NBr	45.38 ± 0.01	58.76	6.35	8.24	9.50	0.8910	0.01
Bu_4NBr	44.93 ± 0.02	61.92	5.17	10.97	8.50	0.9165	0.05
		80 W % Ethylene glycol					
Me_4NBr	43.48 ± 0.03	81.04	5.14	14.76	7.80	0.9366	0.05
Et_4NBr	42.60 ± 0.01	82.91	5.56	13.90	8.20	0.9326	0.01
Pr_4NBr	42.07 ± 0.01	103.60	6.44	15.08	8.95	0.9378	0.01
Bu_4NBr	42.29 ± 0.05	110.84	6.75	15.40	9.20	0.9390	0.04
		90 W % Ethylene glycol					
Me_4NBr	37.07 ± 0.01	87.87	5.78	14.19	7.40	0.9342	0.02
Et_4NBr	37.79 ± 0.05	90.16	5.98	14.06	7.60	0.9336	0.07
Pr_4NBr	36.48 ± 0.02	121.10	7.12	15.99	8.60	0.9411	0.02
Bu_4NBr	37.08 ± 0.01	127.89	6.64	18.24	8.20	0.9480	0.01

Continued...

Table 6 – I continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	K_R	K_S	R A°	α Alpha	σ_Λ %
			100 % Ethylene glycol				
Me_4NBr	35.02 ± 0.01	157.87	9.73	15.21	9.10	0.9383	0.01
Et_4NBr	33.16 ± 0.19	172.80	9.59	17.06	9.00	0.9445	0.32
Pr_4NBr	28.86 ± 0.12	182.37	10.34	16.63	9.50	0.9433	0.01
Bu_4NBr	28.96 ± 0.01	203.39	10.49	18.37	9.60	0.9484	0.01

Table 6–II: Best–fit parameters for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in ethylene glycol–water mixtures at 25° C, using the Justice conductance equation.

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	R_j A°	σ_Λ %
	10 W % Ethylene glycol			
Me_4NBr	100.11 ± 0.07	0.143	4.94	0.07
Et_4NBr	99.65 ± 0.01	4.88	3.15	0.01
Pr_4NBr	91.71 ± 0.07	6.21	3.64	0.06
Bu_4NBr	89.34 ± 0.01	6.75	3.22	0.01
	20 W % Ethylene glycol			
Me_4NBr	91.32 ± 0.06	5.01	4.11	0.06
Et_4NBr	85.11 ± 0.06	7.59	3.49	0.05
Pr_4NBr	75.41 ± 0.05	5.38	5.33	0.04
Bu_4NBr	71.15 ± 0.02	8.58	4.33	0.21
	30 W % Ethylene glycol			
Me_4NBr	75.79 ± 0.05	5.69	2.82	0.04
Et_4NBr	70.82 ± 0.04	9.73	3.10	0.03
Pr_4NBr	62.95 ± 0.05	8.04	4.23	0.04
Bu_4NBr	60.24 ± 0.10	8.52	4.46	0.09
	40 W % Ethylene glycol			
Me_4NBr	64.47 ± 0.03	8.98	3.59	0.02
Et_4NBr	60.07 ± 0.02	11.73	3.65	0.02
Pr_4NBr	55.53 ± 0.05	21.17	3.01	0.04
Bu_4NBr	50.94 ± 0.07	23.73	4.94	0.05

Continued...

Table 6 – II continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	R_j A°	σ_Λ %
	50 W % Ethylene glycol			
Me_4NBr	51.30 ± 0.14	8.74	3.17	0.11
Et_4NBr	48.14 ± 1.08	14.56	10.49	1.00
Pr_4NBr	46.76 ± 0.05	22.69	3.78	0.04
Bu_4NBr	45.60 ± 0.06	28.07	5.65	0.05
	60 W % Ethylene glycol			
Me_4NBr	48.36 ± 0.12	32.64	2.62	0.11
Et_4NBr	46.97 ± 0.02	24.29	3.19	0.02
Pr_4NBr	49.10 ± 0.01	33.33	-14.13	0.01
Bu_4NBr	48.86 ± 0.01	36.77	-14.15	0.01
	70 W % Ethylene glycol			
Me_4NBr	47.20 ± 0.04	38.55	3.14	0.03
Et_4NBr	44.98 ± 0.01	38.75	2.11	0.01
Pr_4NBr	45.23 ± 0.01	47.57	-0.16	0.01
Bu_4NBr	44.68 ± 0.02	51.08	3.69	0.01
	80 W % Ethylene glycol			
Me_4NBr	43.23 ± 0.02	69.62	4.88	0.01
Et_4NBr	42.41 ± 0.01	71.93	3.44	0.003
Pr_4NBr	41.89 ± 0.01	90.66	1.48	0.006
Bu_4NBr	42.09 ± 0.02	96.98	0.224	0.01

Continued...

Table6 – II continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	R_j A°	σ_Λ %
	90 W % Ethylene glycol			
Me_4NBr	36.94 ± 0.01	77.25	5.16	0.01
Et_4NBr	37.41 ± 0.03	79.95	6.77	0.02
Pr_4NBr	36.25 ± 0.01	105.50	4.98	0.01
Bu_4NBr	36.86 ± 0.01	113.21	4.72	0.01
	100 % Ethylene glycol			
Me_4NBr	35.06 ± 0.01	139.13	5.78	0.01
Et_4NBr	33.25 ± 0.14	162.65	-18.53	0.11
Pr_4NBr	28.71 ± 0.01	160.82	5.67	0.004
Bu_4NBr	28.86 ± 0.01	182.63	4.69	0.003

Table 6–III: Best–fit parameters for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in ethylene glycol–water mixtures at 25° C, using the FOS conductance equation.

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
	10 W % Ethylene glycol			
Me_4NBr	100.46 ± 0.14	3.76	2.63	0.14
Et_4NBr	99.43 ± 0.12	3.76	2.33	0.02
Pr_4NBr	91.57 ± 0.35	5.05	2.15	0.08
Bu_4NBr	89.21 ± 0.31	5.80	2.52	0.03
	20 W % Ethylene glycol			
Me_4NBr	91.38 ± 0.18	3.26	1.79	0.08
Et_4NBr	85.09 ± 0.38	5.88	2.30	0.09
Pr_4NBr	75.46 ± 0.10	2.56	0.77	0.06
Bu_4NBr	71.10 ± 0.69	6.64	2.18	0.40
	30 W % Ethylene glycol			
Me_4NBr	75.67 ± 0.18	4.54	2.72	0.07
Et_4NBr	70.77 ± 0.09	8.82	2.91	0.06
Pr_4NBr	62.77 ± 0.24	6.04	1.89	0.09
Bu_4NBr	59.88 ± 0.24	5.70	1.83	0.05
	40 W % Ethylene glycol			
Me_4NBr	64.42 ± 0.06	7.58	2.56	0.06
Et_4NBr	59.94 ± 0.15	10.16	2.68	0.06
Pr_4NBr	55.50 ± 0.10	20.45	3.57	0.13
Bu_4NBr	50.98 ± 0.20	22.45	2.59	0.05

Continued...

Table 6 – III continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
	50 W % Ethylene glycol			
Me_4NBr	51.11 ± 0.04	6.25	2.51	0.04
Et_4NBr	50.56 ± 0.11	19.20	3.46	0.09
Pr_4NBr	46.73 ± 0.10	21.44	3.26	0.15
Bu_4NBr	45.47 ± 0.11	24.42	1.74	0.14
	60 W % Ethylene glycol			
Me_4NBr	48.33 ± 0.15	31.62	3.86	0.28
Et_4NBr	46.94 ± 0.04	23.14	3.62	0.05
Pr_4NBr	49.11 ± 0.03	33.47	4.87	0.07
Bu_4NBr	48.88 ± 0.04	36.93	4.87	0.05
	70 W % Ethylene glycol			
Me_4NBr	47.16 ± 0.09	36.95	3.90	0.09
Et_4NBr	44.97 ± 0.02	37.81	4.35	0.03
Pr_4NBr	45.23 ± 0.05	47.13	4.73	0.05
Bu_4NBr	44.64 ± 0.05	49.25	3.71	0.07
	80 W % Ethylene glycol			
Me_4NBr	43.18 ± 0.09	66.14	3.47	0.08
Et_4NBr	42.38 ± 0.04	69.58	4.16	0.01
Pr_4NBr	41.88 ± 0.11	89.44	4.74	0.05
Bu_4NBr	42.10 ± 0.19	96.28	4.94	0.09

Continued...

Table 6 – III continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
	90 W % Ethylene glycol			
Me_4NBr	36. 86 ± 0.08	71.79	3.69	0.04
Et_4NBr	37.28 ± 0.20	66.83	2.72	0.12
Pr_4NBr	36.21 ± 0.10	100.88	3.93	0.04
Bu_4NBr	36.84 ± 0.04	108.87	4.05	0.01
	100 % Ethylene glycol			
Me_4NBr	34.99 ± 0.18	133.45	5.84	0.14
Et_4NBr	33.00 ± 0.66	151.48	6.55	0.54
Pr_4NBr	28.68 ± 0.13	156.16	6.09	0.11
Bu_4NBr	28.84 ± 0.06	179.70	6.69	0.07

Table 6–IV: Best–fit parameters for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in ethylene glycol–water mixtures at 25° C, using the Pitts conductance equation.

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
	10 W % Ethylene glycol			
Me_4NBr	100.82 ± 0.06	2.33	1.25	0.02
Et_4NBr	99.03 ± 0.07	3.74	2.19	0.04
Pr_4NBr	91.59 ± 0.09	5.72	2.51	0.06
Bu_4NBr	88.88 ± 0.05	5.75	2.35	0.02
	20 W % Ethylene glycol			
Me_4NBr	91.46 ± 0.06	5.08	4.35	0.06
Et_4NBr	84.96 ± 0.17	6.26	2.32	0.06
Pr_4NBr	75.56 ± 0.06	7.73	2.00	0.07
Bu_4NBr	71.36 ± 0.12	7.61	2.01	0.07
	30 W % Ethylene glycol			
Me_4NBr	75.11 ± 0.10	3.74	2.30	0.11
Et_4NBr	70.48 ± 0.08	9.27	2.38	0.08
Pr_4NBr	62.89 ± 0.07	8.40	4.48	0.06
Bu_4NBr	60.19 ± 0.09	9.57	6.21	0.14
	40 W % Ethylene glycol			
Me_4NBr	64.28 ± 0.04	7.61	2.38	0.07
Et_4NBr	59.75 ± 0.05	10.07	2.25	0.05
Pr_4NBr	55.30 ± 0.07	19.22	2.37	0.12
Bu_4NBr	50.89 ± 0.06	25.31	7.88	0.09

Continued...

Table 6 – IV continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
	50 W % Ethylene glycol			
Me_4NBr	50.09 ± 0.04	6.34	2.54	0.09
Et_4NBr	49.80 ± 0.10	15.77	2.29	0.17
Pr_4NBr	46.64 ± 0.05	20.89	2.32	0.10
Bu_4NBr	45.49 ± 0.04	30.15	12.20	0.06
	60 W % Ethylene glycol			
Me_4NBr	48.15 ± 0.09	29.63	2.22	0.60
Et_4NBr	46.75 ± 0.04	21.57	2.23	0.25
Pr_4NBr	48.67 ± 0.08	28.84	2.19	0.46
Bu_4NBr	48.38 ± 0.08	32.02	2.15	0.42
	70 W % Ethylene glycol			
Me_4NBr	46.88 ± 0.05	34.43	2.28	0.27
Et_4NBr	44.56 ± 0.06	33.74	2.29	0.30
Pr_4NBr	44.75 ± 0.07	41.77	2.29	0.34
Bu_4NBr	44.54 ± 0.03	48.07	2.37	0.17
	80 W % Ethylene glycol			
Me_4NBr	43.17 ± 0.04	66.90	2.62	0.17
Et_4NBr	42.06 ± 0.03	65.78	2.39	0.11
Pr_4NBr	41.46 ± 0.05	82.84	2.44	0.18
Bu_4NBr	41.68 ± 0.06	89.09	2.42	0.21

Continued....

Table 6 – IV continued

Salt	Λ_0 (S cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	a° (A°)	σ_Λ %
	90 W % Ethylene glycol			
Me_4NBr	36.76 ± 0.02	71.35	2.66	0.11
Et_4NBr	37.42 ± 0.05	75.23	5.39	0.25
Pr_4NBr	36.14 ± 0.02	100.12	2.67	0.10
Bu_4NBr	36.70 ± 0.02	107.00	2.62	0.07
	100 % Ethylene glycol			
Me_4NBr	34.92 ± 0.01	130.24	3.06	0.11
Et_4NBr	32.89 ± 0.19	145.07	3.19	0.13
Pr_4NBr	28.62 ± 0.04	152.47	3.11	0.11
Bu_4NBr	28.75 ± 0.01	172.83	3.13	0.11

$75.60 \geq D \geq 66.60$, the extent of change in Λ_0 values is quite significant. This is in agreement with the earlier findings[17, 81, 90 - 98, 116] in several pure and mixed solvents. Although, the decrease in Λ_0 values with increasing proportion of ethylene glycol can also be explained on the basis of ion-solvent interactions, the increase in their value may be due to an increase in the ionic size and the hydrophobic solvation of cations, the order being $Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+$. It may, consequently, support a decrease in the mobility of the respective ions in the reverse order. These observations are mainly due to the predominant role played by the viscosities of the medium in determining an overall behavior of ionic mobilities. An increase in viscosity[117] with increase in the ethylene glycol content in EG–H_2O mixtures indicate the structure breaking effect of the components on each other. However, ethylene glycol despite possessing a higher degree of self-association through hydrogen bonding does not have a defined geometric structure[118, 119] due to autoprotolysis[120] of ethylene glycol water system. Therefore, the incompatibility arises due to dissimilarity in the basic geometric structure, as well as the differences in hydrogen bond energies, which result in the breakage of the structural integrities of ethylene glycol and water. This also seems to be due to the fact that the individual water molecules will get themselves loosely associated with ethylene glycol molecules through hydrogen bonding resulting in the less structured solvent mixture than that expected from the ideal behavior.

Association Constant

The values of K_A (Table 6) computed for all the salts in EG+H_2O mixtures through the F78 equation have been found to be larger than those obtained from the J, P and FOS equations. The average percentage difference in the K_A value obtained by using F78 equation and those obtained by the J, P and FOS equations are ~ 24.59 %, ~ 29.18 % and ~ 28.63 %, respectively. It appears from Table 6 that K_A values increase with decrease in the dielectric constant of the medium and in a given dielectric medium K_A increases with increase in the size of the cations in the order, $Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+$ as also reported earlier[100-102, 106] for similar systems.

The applicability of the various theories of ion association can be examined in terms of the dependence of log K_A versus 1/D (Fig. 7). The non-linearity of the plot suggests the applicability of F78, J, P and FOS theories of ionic association. Such plots in EG+H_2O mixtures resemble with those in methanol-water mixtures[121] in the water-rich region but deviate in somewhat higher organic solvent content medium. However, this suggests that the tetra-alkyl-ammonium ions contribute toward association by the formation of solvent-separated ion pair in the solvents of low dielectric constant medium.

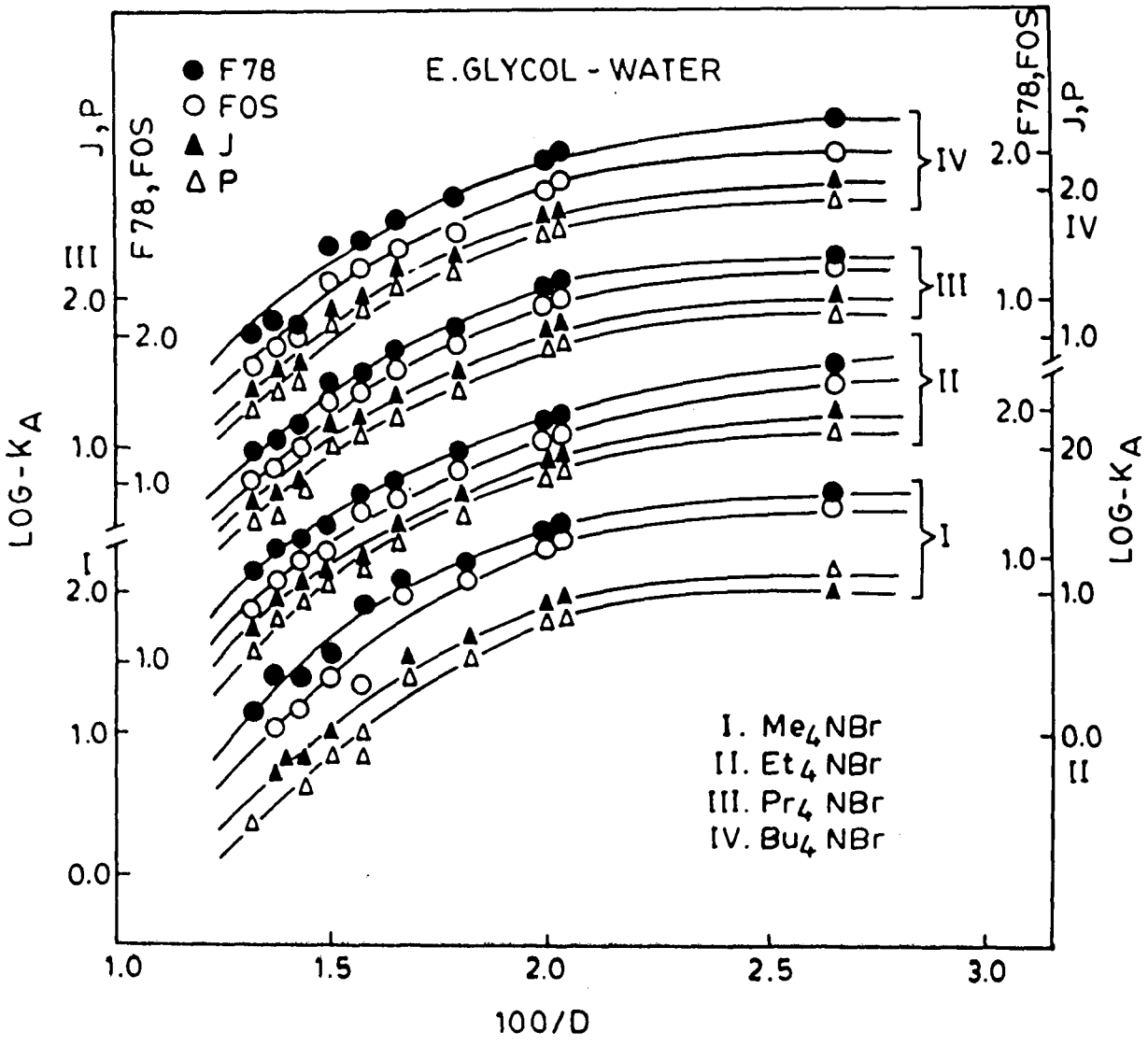

FIG. 7. PLOTS OF LOG K_A Vs 1/D.

Moreover, an increase in the ionic association with increase in the proportion of ethylene glycol may be ascribed to the predominant solvation of cations with one of the solvent mixtures, which seem to control the extent of ion pairing. The values of K_A obtained in EG+H_2O mixtures are found to be less than those obtained in dioxane-water mixtures (cf. chapter I). The difference seems to be due to the interaction between oppositely charged ions other than the coulombic attraction (of opposite charges) and hence stabilizes the contact ion pair. Masterton et al[122] suggested that the extra stability of the associated species comes from a dispersion interaction.

D'Aprano and Fuoss[123] interpreted the high association constant of TiCl in dioxane-water mixture by calculating the energies due to the interaction between the charges and the induced dipoles. Similarly, tetra-alkyl-ammonium ions show extra stability of associated species, which may in some cases give higher values of K_A in lower dielectric medium[11].

Distance and Ion-Size Parameter

The values of R computed using Fuoss method of analysis by minimizing the standard deviation, σ,

$$\sigma = \sum_i \{[\Lambda_{i(cal)} - \Lambda_{i(obs)}]^2 / n - 2\}^{1/2}$$

for the sequence of R values and then plotting σ_Λ % (= σ_{min} x 100/ Λ_0) against R the best fit R_{min} corresponds to the minimum in the σ_Λ % - R curve. However, the course of scan using unit increment of R value (Table 7) gives minimum in the σ_Λ % - R curve. For a given dielectric constant (D = 66.60) the plots of σ_Λ % versus R (Fig. 8) show a shallow minimum for Me_4NBr and Pr_4NBr while a sharp minimum for Et_4NBr and Bu_4NBr.

The distance parameter or Gurney cosphere diameter, R (Table 6-I) obtained from the F78 equation for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr are found to be larger compared to those of the distance of closest approach, R_j (Table 6-II) and the ion size parameter, a° (Table 6-III and 6-IV) calculated from the J, P and FOS equations, respectively. The values of the distance or the ion size parameters obtained in EG+H_2O mixtures from J, P and the FOS equations are smaller than the crystallographic radius of the ion-pair which explain the inadequacy of the theories. However, the R values computed through the F78 equation appear to be reasonable and are found to be higher than the Bjerrum distance, q (= e^2 / 2 DKT) whereas $R_j \leq q$ and a° are less than q. However, a perusal of Table 6-I reveals that the values of R for all the salts increase with a decrease in the dielectric constant of the medium which indicates an increase in the ionic-

Table 7: Variation of R with σ_Λ % for Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr in 60 % ethylene glycol – water mixture.

Me_4NBr		Et_4NBr		Pr_4NBr		Bu_4NBr	
R	σ_Λ %	R	σ_Λ %	R	σ_Λ %	R	σ_Λ %
7.1	0.2135	6.30	0.0406	9.8	0.2248	9.1	0.0189
7.2	0.2183	6.45	0.0402	9.9	0.2242	9.2	0.0169
7.3	0.2133	6.60	0.0398	10.0	0.2238	9.3	0.0153
7.4	0.2132	6.75	0.0394	10.1	0.2233	9.4	0.0143
7.5	0.2132	6.90	0.0392	10.2	0.2230	9.5	0.0142
7.6	0.2132	7.05	0.0390	10.3	0.2228	9.6	0.0149
7.7	0.2132	7.20	0.0390	10.4	0.2226	9.7	0.0165
7.8	0.2132	7.35	0.0392	10.5	0.2226	9.8	0.0186
7.9	0.2133	7.50	0.0393	10.6	0.2226	9.9	0.0215
8.0	0.2135	7.65	0.0402	10.7	0.2227	10.0	0.0245
8.1	0.2137	7.80	0.0411	10.8	0.2229		
8.2	0.2139			10.9	0.2232		
				11.0	0.2236		

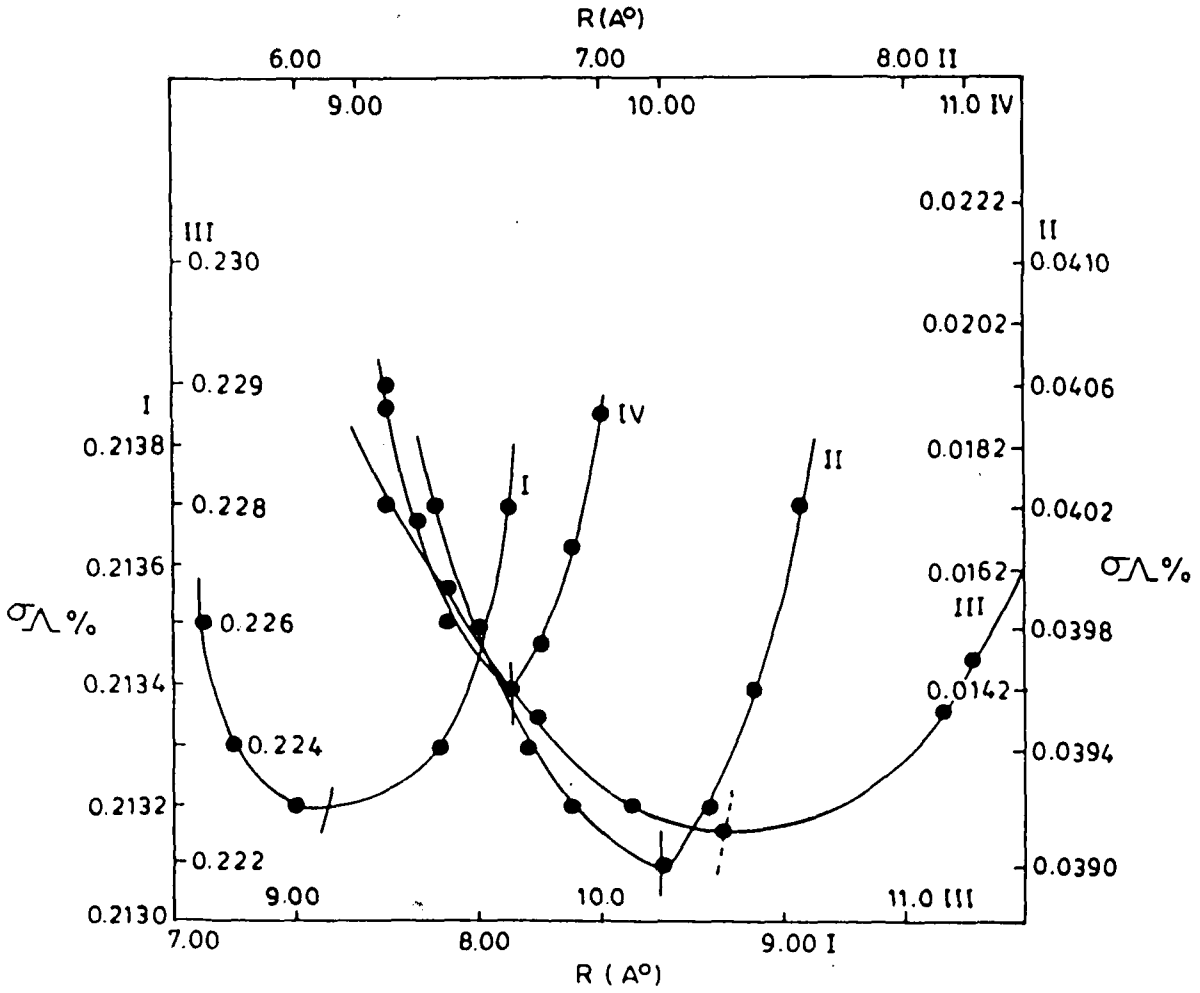

FIG. 8. PLOTS OF σΛ % Vs R(A°) FOR (I) Me_4NBr, (II) Et_4NBr, (III) Pr_4NBr AND (IV) Bu_4NBr IN 60 % EG-WATER MIXTURE.

association[24, 74, 122] and such a behavior can also be explained by the formation of the SSIP and CIP which has already been given in the case of dioxane-water mixture (cf. Chapter I), for a contact ion-pair (CIP), R = a, and for SSIP, R = a + ds, where ds is the diameter of the solvent molecule. Therefore, the values of R show that the tetra-alkyl-ammonium halides (Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr) from CIP in the cases of 10, 20 30 W % EG while in the cases of 40 and 50 W % EG only Me_4NBr, Et_4NBr and Pr_4NBr form CIP but Bu_4NBr form SSIP. In the dielectric range ($59.4 \geq D \geq 37.7$), ion-pairs are mostly formed as SSIP.

The variation in the pairing radius R with the reciprocal of the dielectric constant of the solvent mixture is shown in Fig. 9, in which the dotted line represents the variation Bjerrum radius (β / 2). The perpendicular lines in these plots (Fig. 9) show the limiting values of R corresponding to the minimum in σ_Λ % and the circles corresponds to the best values, (i.e. $\sigma = \sigma_{min}$).

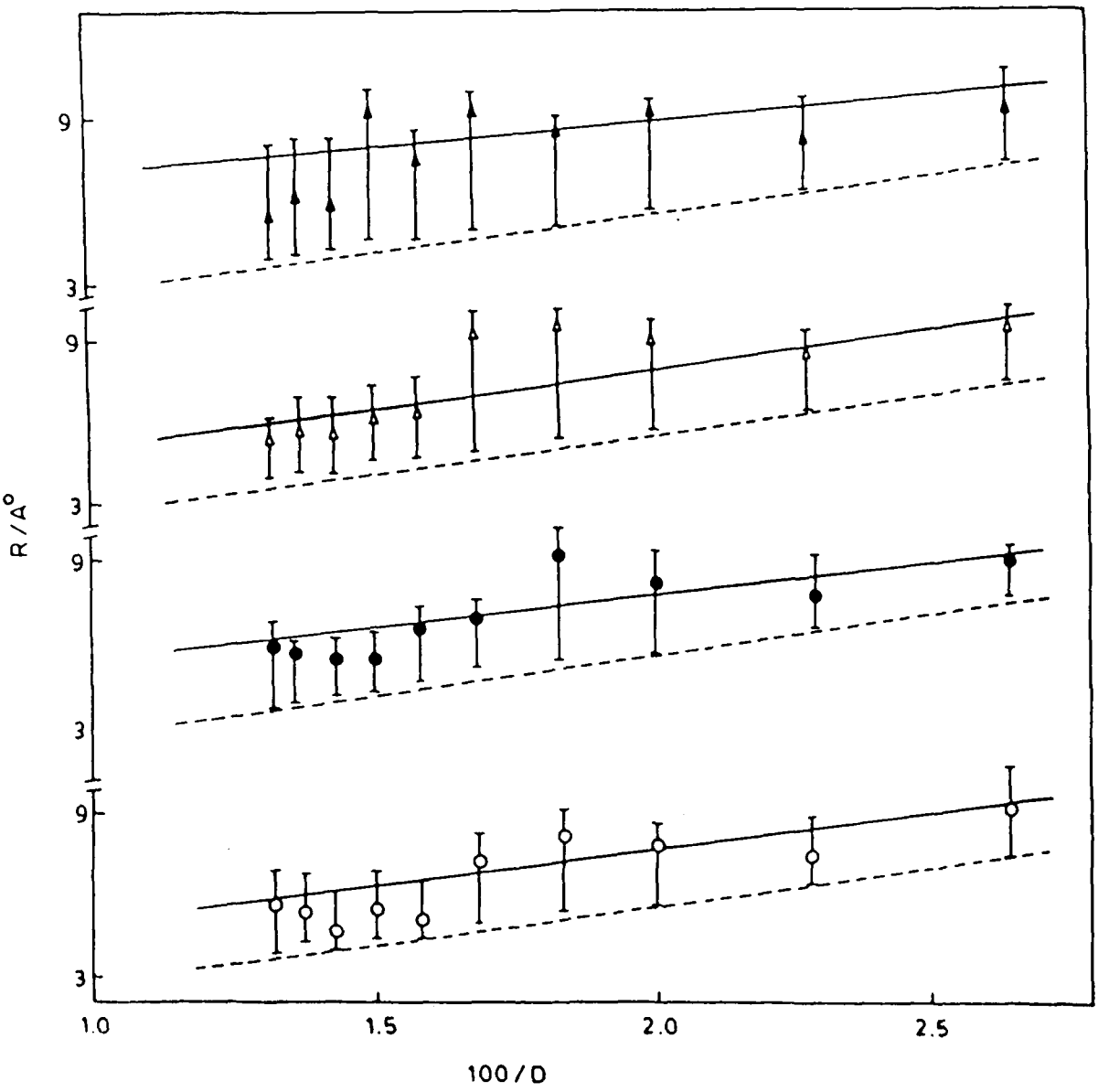

FIG.9. VARIATION OF PAIRING RADIUS R WITH RECIPROCAL OF THE DIELECTRIC CONSTANT OF THE SOLVENT MIXTURES. ○ Me_4NBr, ● Et_4NBr, Δ Pr_4NBr AND ▲ Bu_4NBr. DOTTED LINE REPRESENTS $\beta/2$.

PART – B

APPARENT MOLAR VOLUMES AND VISCOSITIES OF ELECTROLYTIC SOLUTIONS IN ETHYLENE GLYCOL WATER MIXTURES

INTRODUCTION

The density and viscosity of pure solvents and of concentrated electrolytic solutions[1-4, 55, 124, 125] have been studied. It has been found that tetra-alkyl salts have got good solubility characteristic in many solvents. Therefore, different methods[136, 137] are employed to obtain information about the nature of mixed solvents and the behavior of electrolytes in them.

In order to understand the ion-solvent interactions in non-aqueous solvents[9, 126-138], the apparent molar volumes of electrolytes have been calculated[78] for several concentrations of electrolytic solutions from the corresponding density data,

$$\varphi_v = \frac{M}{d_0} - \frac{1000(d-d_0)}{d_0 C} \qquad (1)$$

where d_0 and d are the densities of solvent and of solution respectively, M is the molecular weight of the solute, and C is the molar concentration.

According to Masson equation[139], the apparent molar volume is a linear function of square root of molar concentration and this relation,

$$\varphi_v = \varphi_v^0 + S_v\sqrt{C} \qquad (2)$$

often extends to even the concentrated solution[78, 131, 139]. φ_v^0 is the apparent molar volume at infinite dilution, which is obtained by the extrapolation of φ_v data to zero concentration, and S_v is the experimental slope. It is an empirical quantity and can give some indication of the ion-ion interaction.

The concentration dependence of viscosity for the electrolytic solutions was explained by Jones-Dole[5] viscosity equation,

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \qquad (3a)$$

or the specific viscosity relation,

$$\eta/\eta_0 - 1 = A\sqrt{C} + BC \qquad (3b)$$

where η and η_0 are the viscosities of the solution and the pure solvent, respectively. A and B are the constant for the given solute-solvent system. The B-coefficient of the Jones-Dole viscosity equation in non-aqueous media is positive. The coefficient A is due to the contribution from inter-ionic electrostatic forces[37, 38, 140] and B gives a measure of the order or disorder introduced by the ion into the solvent structure. Therefore, B-coefficient shows ion-solvent interaction. It is highly

specific additive in nature[141] and because of this it depends on the constituent ions of the solute. Thus

$$B = Z_+B_- + Z_-B_+$$

where $Z_\pm B_\pm$ refers to the product of ionic valence and ionic viscosity coefficient. The value of ionic B coefficient for several cations and anions are given in the literature[9, 104, 142-144]. Jones-Dole viscosity equation is applicable only to dilute solution concentration range of 0.002 M to 0.2 M. However, Nightingale[6], Millar and Doran[7] investigated the viscosities of concentrated solutions of electrolytes, employing the Eyring[145] treatment of viscosity, based on the theory of rate processes.

Density and viscosity data of several systems reported recently[146-148] were analyzed in terms of essentially Jones-Dole equation, which has been found suitable in explaining the behavior of interaction. In the present study, measurements of density and viscosity of ethylene glycol-water mixtures and of their solutions with tetra-methyl ammonium-bromide (Me_4NBr) have been made at several temperatures to understand the ion-solvent and the ion-ion interactions.

RESULT AND DISCUSSIONS

Densities and viscosities of ethylene glycol-water mixtures of 10, 20, 30, 40, 50 and 60 % glycol by weight and those of their solutions with tetra-methyl ammonium-bromide have been studied as functions of temperature and concentration. The temperature dependence of density of solvent mixtures and their solutions with Me_4NBr have been explained by the usual linear equation,

$$\rho = a + bT \qquad (4)$$

The computed values of a and b for different solutions are given in Table 1.

It has been observed that the values of the negative slope 'b' decrease with increasing concentration and 'a' values continuously increase from 10 to 60 % solvent mixtures. The values of standard deviation are quite large in the case of 10 % (especially in 0.2028 and 0.4527 M), 20, 30 and 40 % ethylene glycol-water mixture.

Therefore, in the cases of 20, 30 and 40 % solvent mixtures weaker solvent-solvent interactions are expected, and lower values of standard deviation in concentrated solutions contribute to strong solute-solvent and solvent-solvent interactions.

Table 1: Computed parameters of equation (4) in 10, 20, 30, 40, 50 and 60 W % ethylene glycol–water mixtures.

Concentration	$-b \times 10^3$	a	$SD \times 10^3$
	10 W % Ethylene glycol		
0.0000	0.4445	1.022	0.34
0.2514	0.4586	1.033	0.43
0.3025	0.4321	1.033	0.32
0.3542	0.4422	1.036	0.27
0.4035	0.4499	1.038	0.28
	20 W % Ethylene glycol		
0.2018	0.5158	1.044	0.59
0.3025	0.4580	1.045	0.19
0.3532	0.4582	1.048	0.25
0.4045	0.4602	1.050	0.17
0.4532	0.4556	1.051	0.19
	30 W % Ethylene glycol		
0.2028	0.4782	1.055	0.17
0.2544	0.5012	1.058	0.16
0.3065	0.4914	1.059	0.15
0.3542	0.4864	1.060	0.17
0.4035	0.4886	1.062	0.13
0.4516	0.5076	1.064	0.15

Continued...

Table 1 continued

Concentration	$-b \times 10^3$	a	SD x 10^3
	40 W % Ethylene glycol		
0.2008	0.5508	1.069	0.097
0.2516	0.5438	1.070	0.089
0.3025	0.5423	1.072	0.10
0.3524	0.5570	1.074	0.14
0.4019	0.5472	1.076	0.10
0.4512	0.5444	1.078	0.19
	50 W % Ethylene glycol		
0.0000	0.5981	1.076	0.12
0.2028	0.6003	1.083	0.10
0.2514	0.5959	1.085	0.075
0.3011	0.5855	1.085	0.12
0.3542	0.5864	1.087	0.097
0.4035	0.592	1.089	0.12
0.4467	0.6946	1.089	0.095
	60 W % Ethylene glycol		
0.0000	0.6385	1.089	0.097
0.2000	0.6325	1.095	0.099
0.2500	0.6262	1.096	0.10
0.3000	0.6259	1.097	0.10
0.3500	0.6133	1.099	0.10
0.4620	0.6185	1.100	0.066

The viscosities (Table 2) of solvent mixtures have been plotted against mol % of ethylene glycol in Fig. 1. It is evident that the viscosities of solvent mixtures increase continuously with increase in mol % of the corresponding solution as well as pure solvent, but the plot of η_0 versus mol % is not linear.

Concentration Dependence of Densities

There is an increase in the density of solvent mixture on addition of Me_4NBr, thus apparent molar volumes (φ_v) have been calculated from the corresponding density values by employing eqn. (1).

Three major equations[78, 131] have been available for the extrapolation of the apparent molar volumes. The simplest is eqn. (2), in which the observed φ_v values in the concentration range from 0.15 to 0.5 M have been plotted against the square root of concentration (Figs. 2.1 to 2.6) and by extrapolating the data to zero concentration, apparent molar volumes at infinite dilution (φ_v^0 = the partial molar volumes at infinite dilutions, V_2^0) have been found. The values of φ_v^0's and S_v's at several temperatures (25° to 50° C) are listed in Table3. The limiting experimental slope (S_v) of eqn. (2) in 10 and 20 % Me_4NBr solutions at almost all temperatures is negative and continuously decreases with increase in temperature, suggesting

Table 2: Physical properties of ethylene glycol–water (EG – H_2O) mixtures at 25° C

Mol % of EG	σ (Kg m^{-3} x 10^3)	η (Kg m^{-1} S^{-1} x 10^3)
3.10	1.0117	0.01140 (0.01140)
6.70	1.0262	0.01450 (0.01450)
11.00	1.0384	0.01646 (0.0183)
16.10	1.0500	0.02104 (0.0239)
22.50	1.0611	0.02721
30.10	1.0669	0.04785 (0.0413)
40.36	1.0797	0.05310
53.70	1.0892	0.06751 (0.0795)
72.29	1.0978	0.114035
100.00	1.1013	0.13615 (0.1690)[+]

[+] Ref. 76

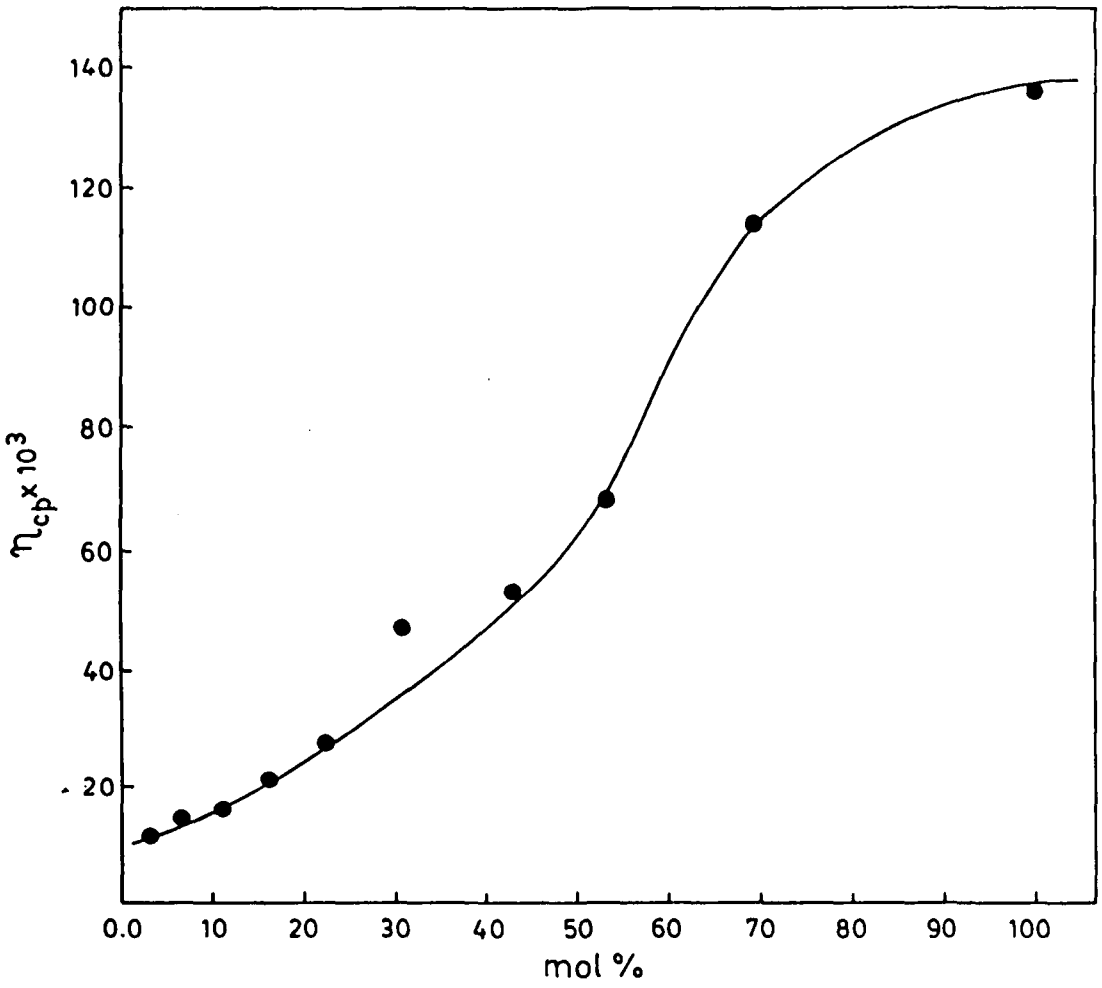

FIG.1. VISCOSITIES OF ETHYLENE GLYCOL - WATER MIXTURES AS A FUNCTION OF MOL % OF ETHYLENE GLYCOL AT 25°C.

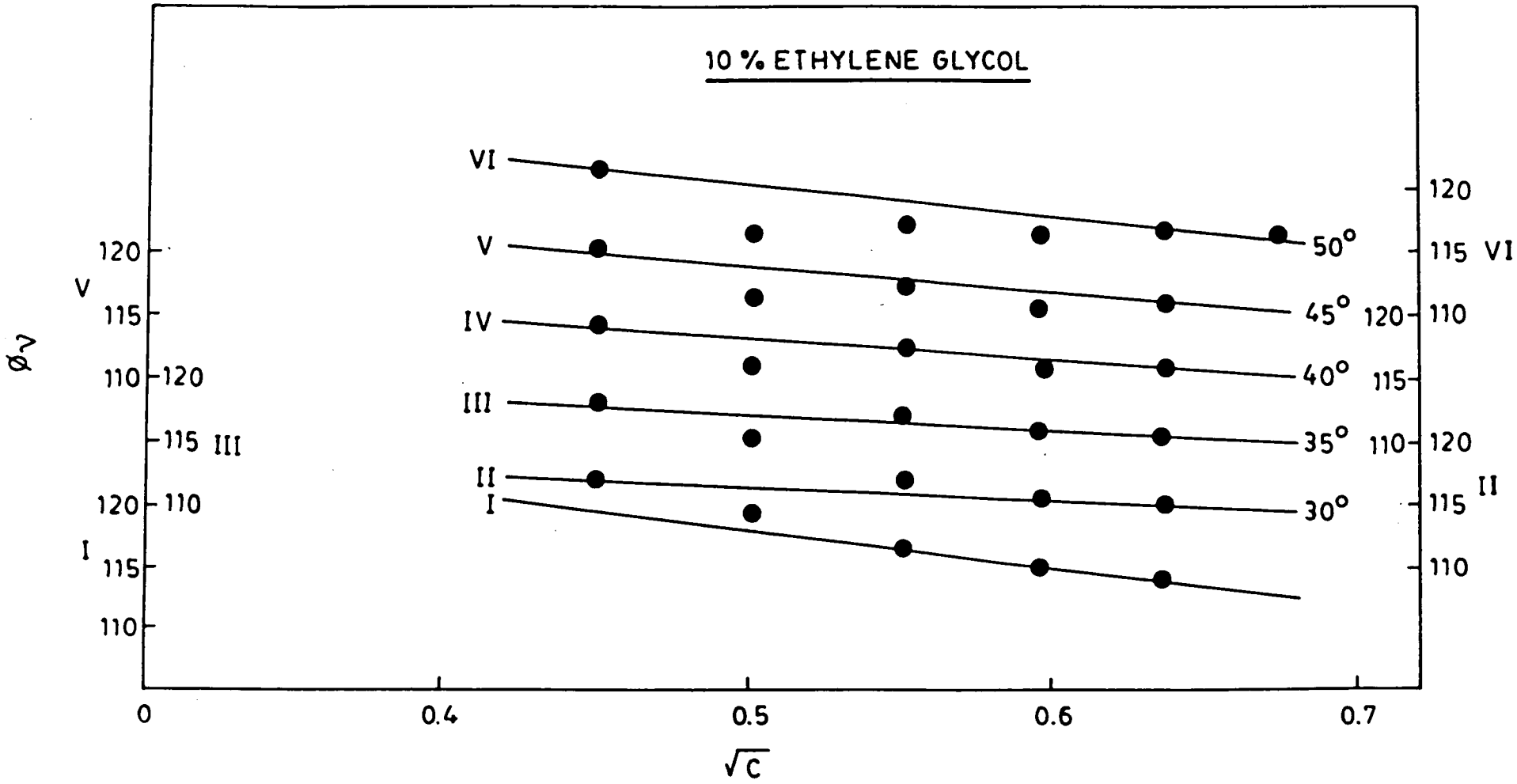

FIG.2.1. PLOTS OF ϕv Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL-WATER MIXTURE.

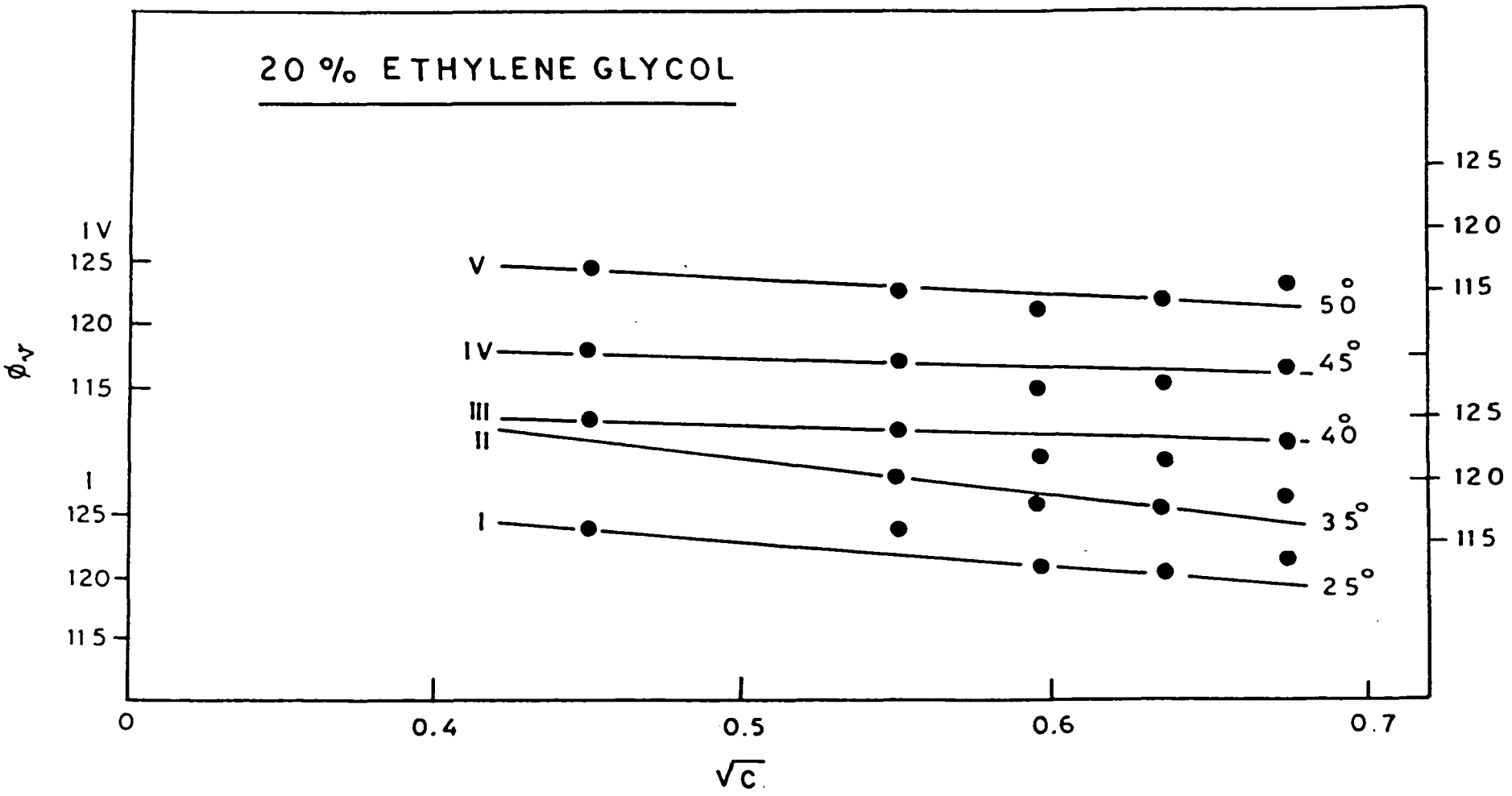

FIG.2.2. PLOTS OF ϕv Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL-WATER MIXTURE.

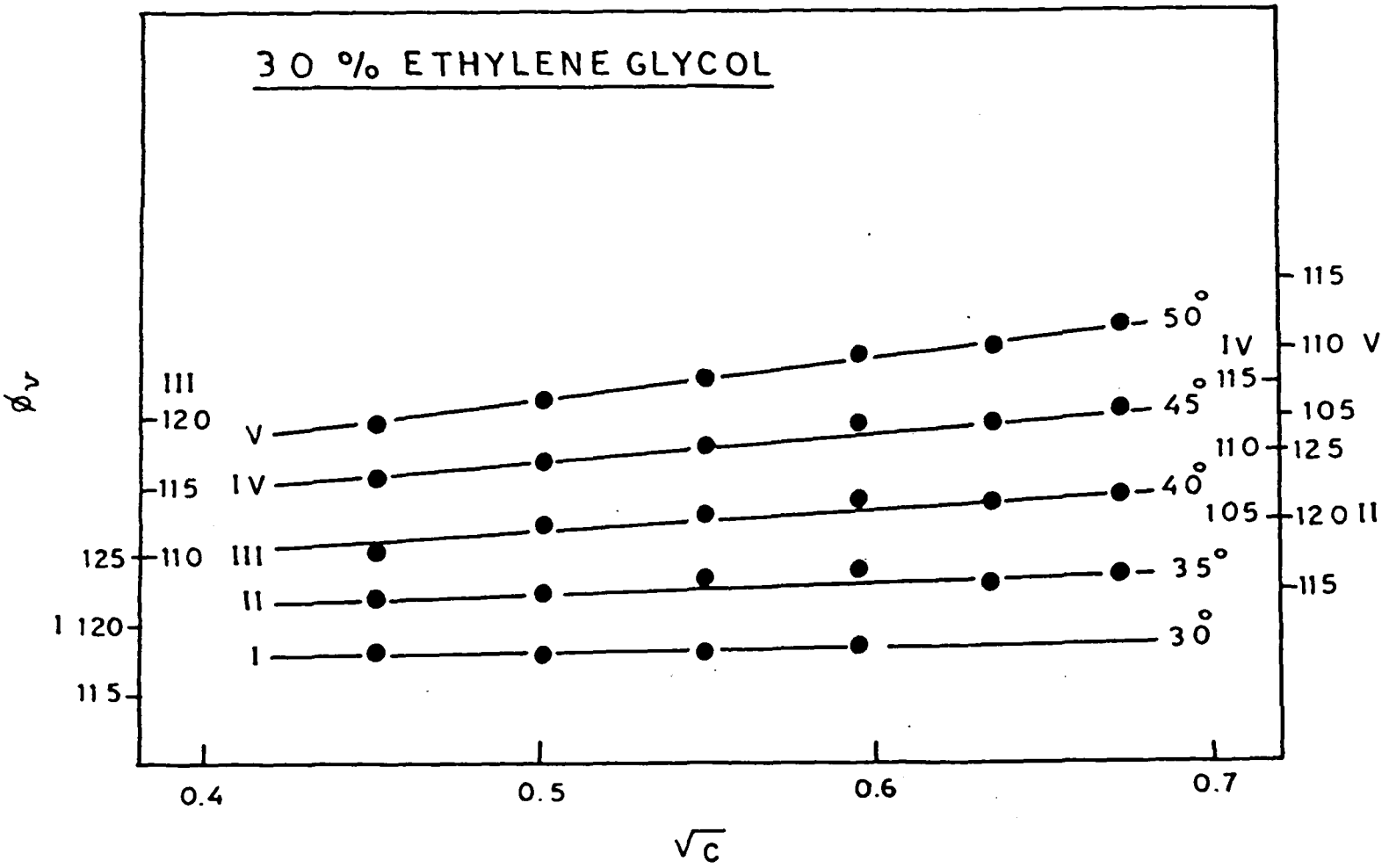

FIG.2.3. PLOTS OF ϕ_v Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL - WATER MIXTURE.

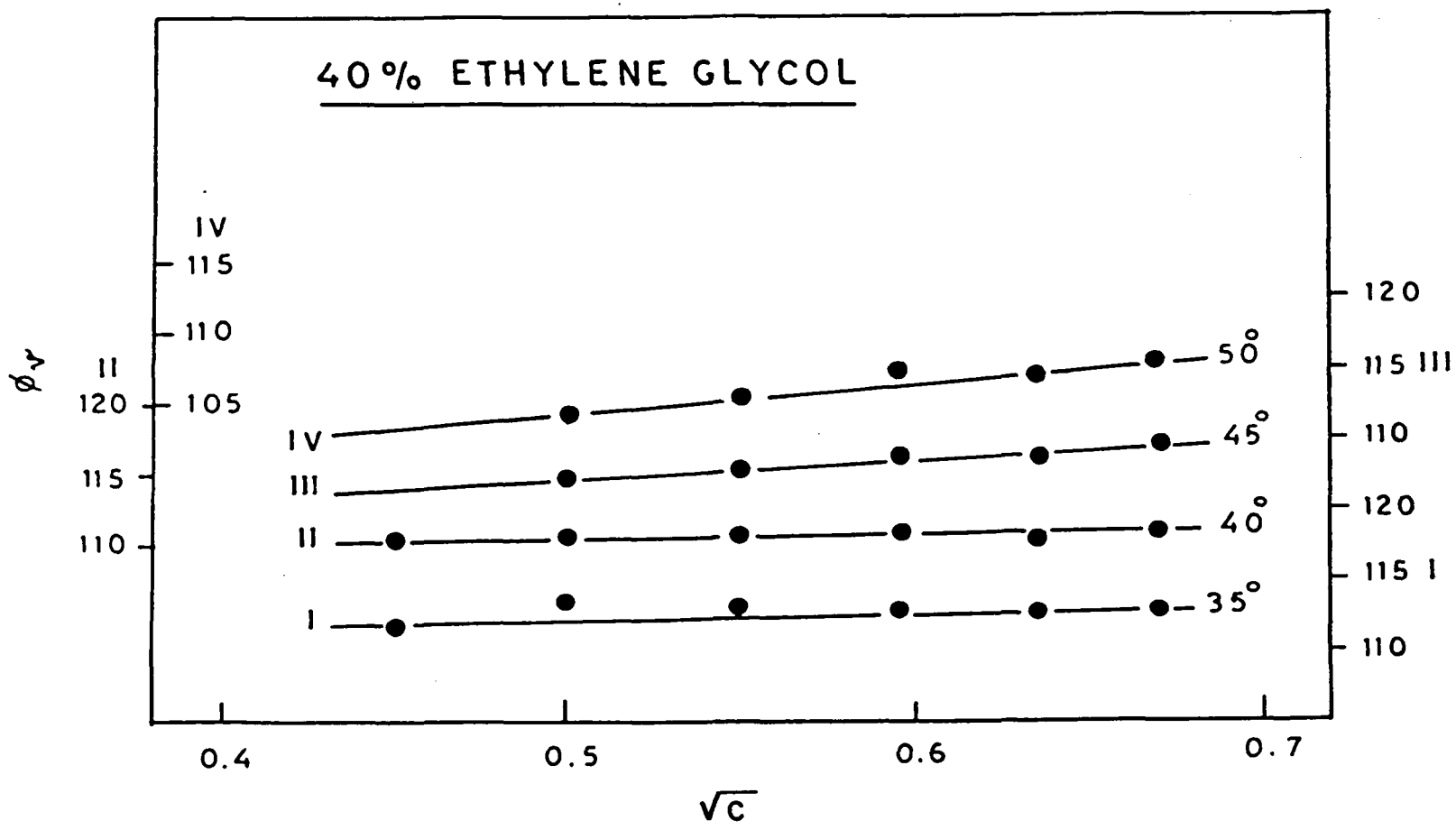

FIG.2.4. PLOTS OF ϕv Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL - WATER MIXTURE.

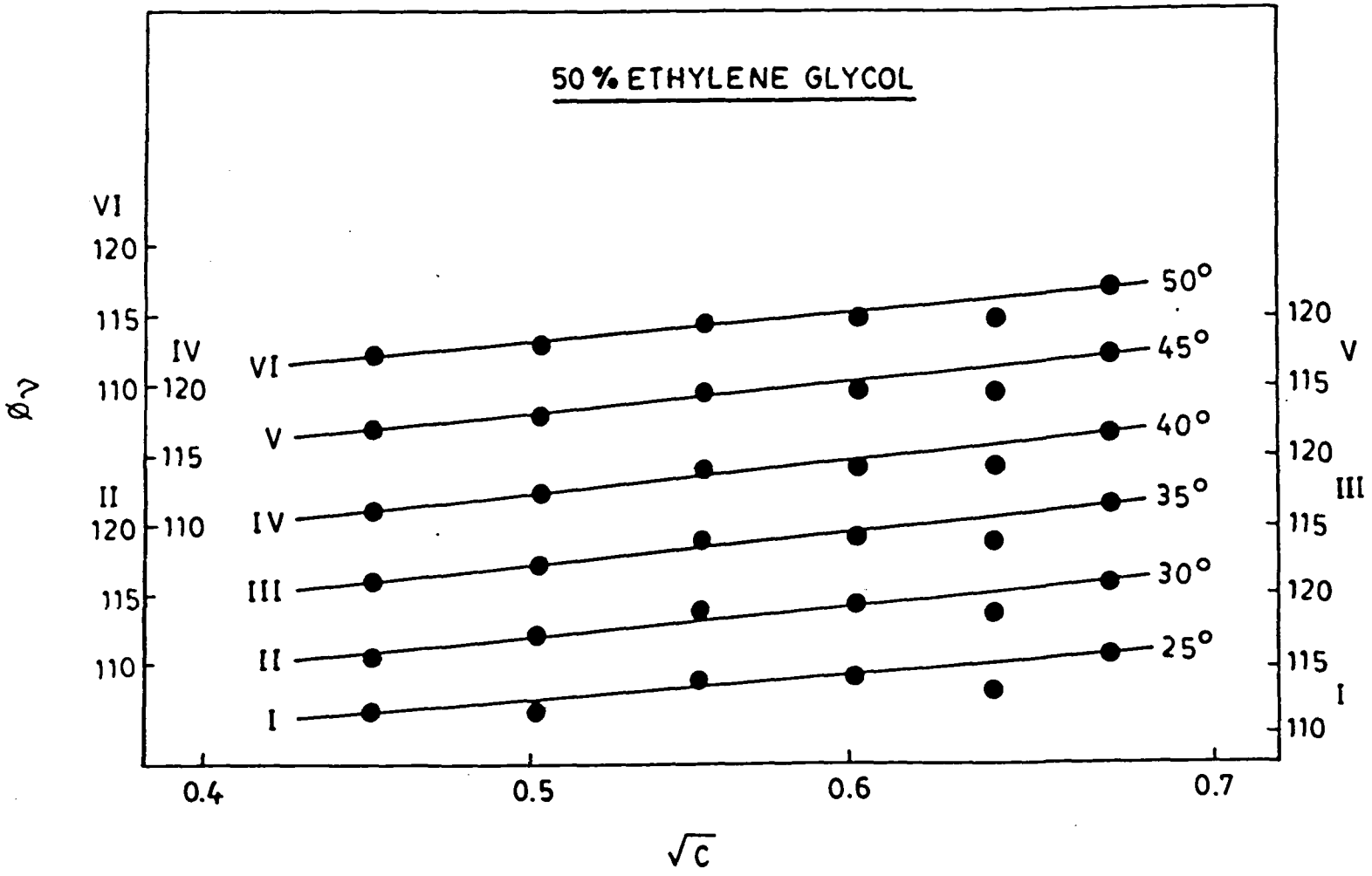

FIG.2.5. PLOTS OF ϕ_V Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL-WATER MIXTURE.

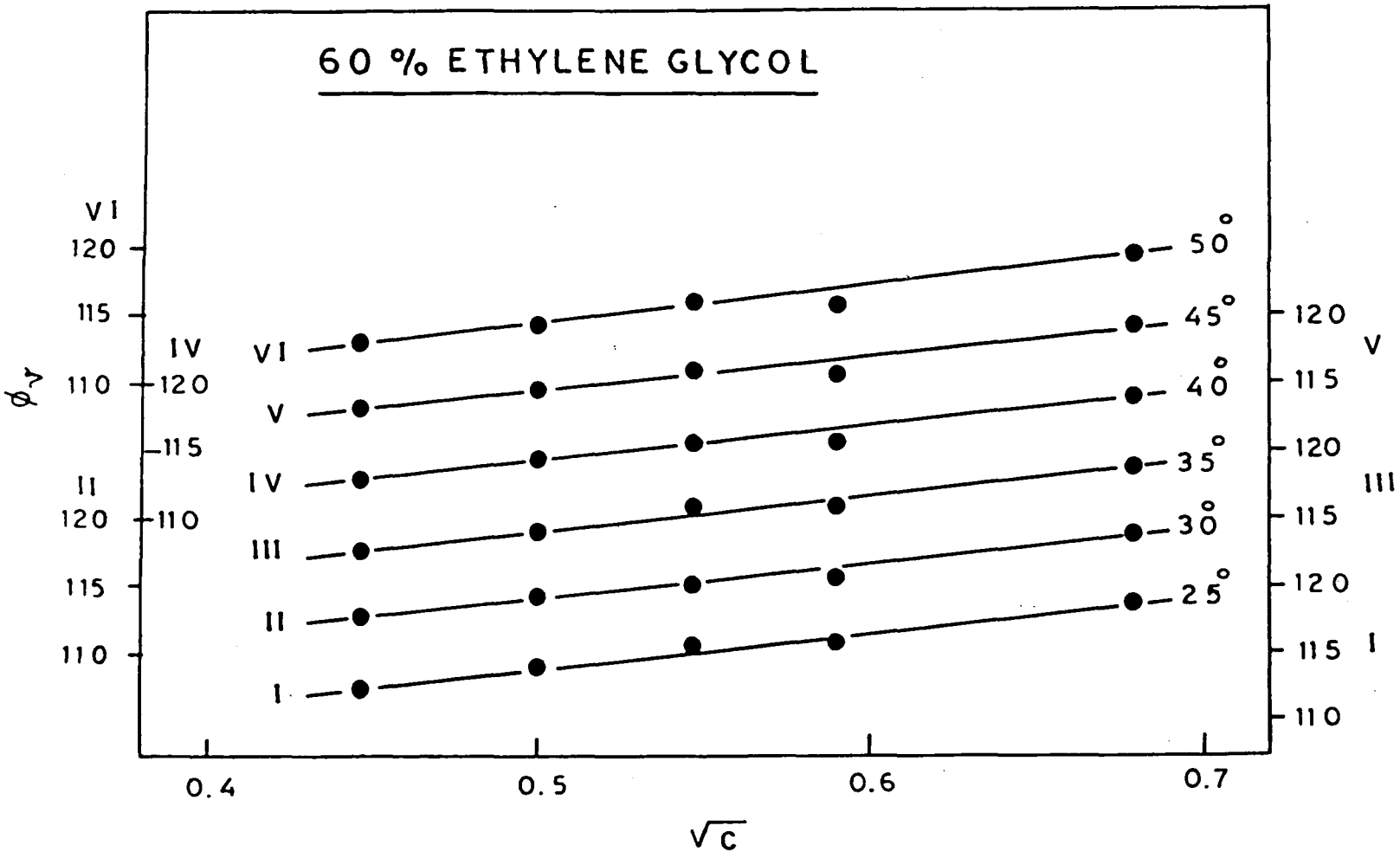

FIG.2.6. PLOTS OF ϕ_v Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL - WATER MIXTURE.

Table 3: Computed Parameters of eqn. (1) in 10, 20, 30, 40, 50 and 60 Wt % Ethylene glycol–water mixtures.

Temperature	φ_v^0	S_v	SD
	10 W % Ethylene glycol		
25	149.0	-66.3	7.25
30	145.9	-58.9	5.75
35	141.6	-48.7	4.20
40	137.2	-38.9	2.27
45	131.9	-27.8	1.49
50	128.0	-18.7	1.61
	20 W % Ethylene glycol		
25	132.9	-18.6	1.12
30	95.5	37.5	3.20
35	161.6	68.6	3.14
40	125.3	-12.5	0.93
45	122.5	-10.4	0.99
50	121.2	-10.3	1.04
	30 W % Ethylene glycol		
25	129.5	-15.6	0.32
30	120.2	-38.7	0.34
35	111.4	7.51	0.40
40	102.1	19.1	0.58
45	92.5	31.4	0.85
50	83.9	42.5	1.08

Continued...

Table 3 continued

Temperature	φ_v^0	S_v	SD
	40 W % Ethylene glycol		
25	128.9	-19.4	0.61
30	119.7	-7.88	0.76
35	112.2	1.37	0.71
40	103.2	12.4	0.99
45	94.1	23.9	0.99
50	85.5	34.7	1.19
	50 W % Ethylene glycol		
25	102.5	18.9	0.98
30	101.5	20.8	0.78
35	101.9	20.6	0.78
40	101.8	21.1	0.80
45	103.0	19.9	0.74
50	103.5	19.3	0.64
	60 W % Ethylene glycol		
25	101.1	25.3	0.35
30	101.6	24.6	0.44
35	101.0	25.7	0.49
40	101.8	24.7	0.51
45	102.2	24.0	0.64
50	101.6	25.2	0.63

thereby weaker ion-ion interactions. Lamb and Lee[149] attributed this effect to hydrolysis, and Geffcken and Price[150] estimated its numerical magnitude at each experimental concentration.

Furthermore, it may be noted that large negative values of the slope (S_v)[125] seem to be responsible for higher standard deviations in the cases of 10 and 20 % ethylene glycol-water mixtures (Table 3). However, in the cases of 30 and 40 % solutions the values of S_v are negative at 25° and 30° C while they are positive between 35° and 50° C, and increase continuously with increasing temperature. This indicates strong electrostatic ion-ion interaction. These experimental results suggest that the ion-ion interactions are weak at low temperatures but increase with increase in temperature.

It is found that the value of φ_v^0's continuously increases with increasing temperature in the cases of 10 to 40 % solutions as apparent from Table 3. Therefore, ion-ion interactions are strongest in the temperature range 25° to 50° C. But in the cases of 50 and 60 % Me_4NBr solutions the values of φ_v^0's are almost constant throughout the temperature range (Table 3) and it may be concluded that these φ_v^0's values correspond to a maximum. Therefore, in the cases of 50 and 60 % Me_4NBr solutions the solute-solvent interactions are stronger than those of the ion-ion interactions in the temperature range 25° to 50° C.

In the present study, it has been found that the character of a proton in different concentrations however is unique and draws much attention as such. In water the primary species are H_3^+O and in glycol, $HOROH_2^+$ but, how the proton is distributed amongs the molecules at a mixed solvent is not yet known without the knowledge of this distribution, structural arguments remain therefore, only conjectural.

It has been found[151] that the electrostriction is maximum in the pure ethylene glycol, and as a result of addition of water, the electrostrictive volume decreases. Because of the interaction of water molecules with those of the glycol, inter-ionic attraction is undoubtedly higher in the ethylene glycol than in water due to the lower dielectric constant of glycol (D_{EG} = 37.7, D_W = 78.5). It has been observed that the value of S_v becomes higher in 60 % ethylene glycol-water mixtures and decreases with the increasing amount of water in the solvent composition, but rises again after reaching a minimum. It is considered that ion-ion interactions can be affected by the influence of ions on the structure of the solvent, as apparent from the occurrence of maximum φ_v^0 and minimum S_v in the cases under discussion.

Concentration Dependence of Viscosities

There is also an increase in the viscosity of solvent mixtures on addition of Me_4NBr. The concentration dependence of viscosity of

electrolytic solutions is described by the Jones-Dole semi-empirical equation[5], within the concentration range, 0.15 to 0.5 M,

$$[(\eta/\eta_0)-1]/\sqrt{C} = A + B\sqrt{C} \qquad (3b)$$

where the A coefficient determined by ion-ion electrostatic interaction can be calculated from the ionic interaction theory by the Falkenhagen-Vernon equation and the B-coefficient is an empirical constant determined by the ion-solvent and the solvent-solvent interactions. This means that the ionic B-coefficient is a measure of solvation effects, ionic influence on solvent structure and the hydrodynamic effects, which are conditioned by the ionic size and the shape.

The linear plot of the function, $(\eta/\eta_0 - 1)/\sqrt{C}$ versus C shown in Figs. 3.1 to 3.5 support the applicability of this equation in the concentration range studied.

It is found from Table 4 that the value of B-coefficients does not increase continuously with temperature. However, an overall decrease in the value of B-coefficient with increasing temperature has been recorded from 25° to 50° C.

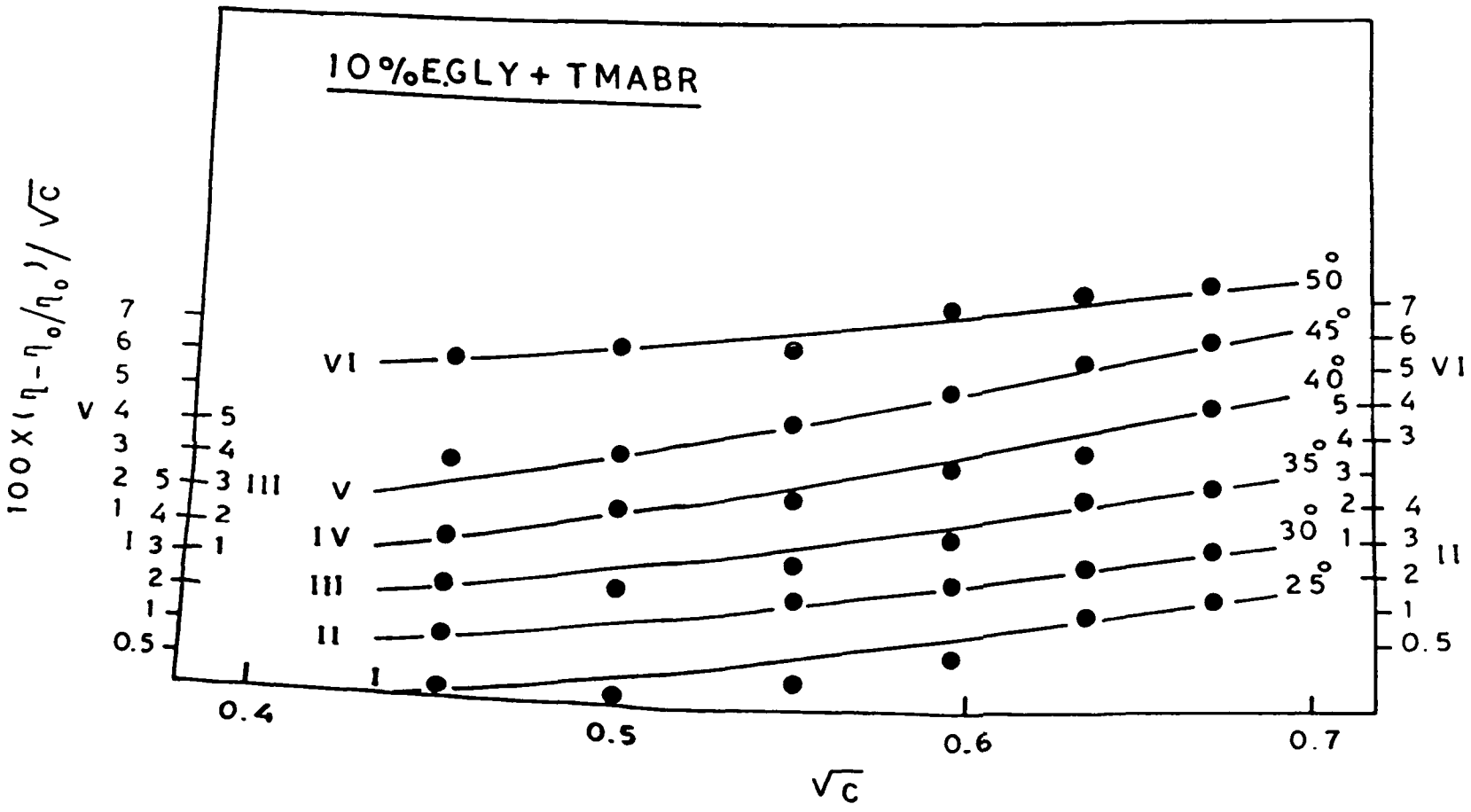

FIG. 3.1. PLOTS OF $(\eta/\eta_o - 1)/\sqrt{C}$ Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL - WATER MIXTURE.

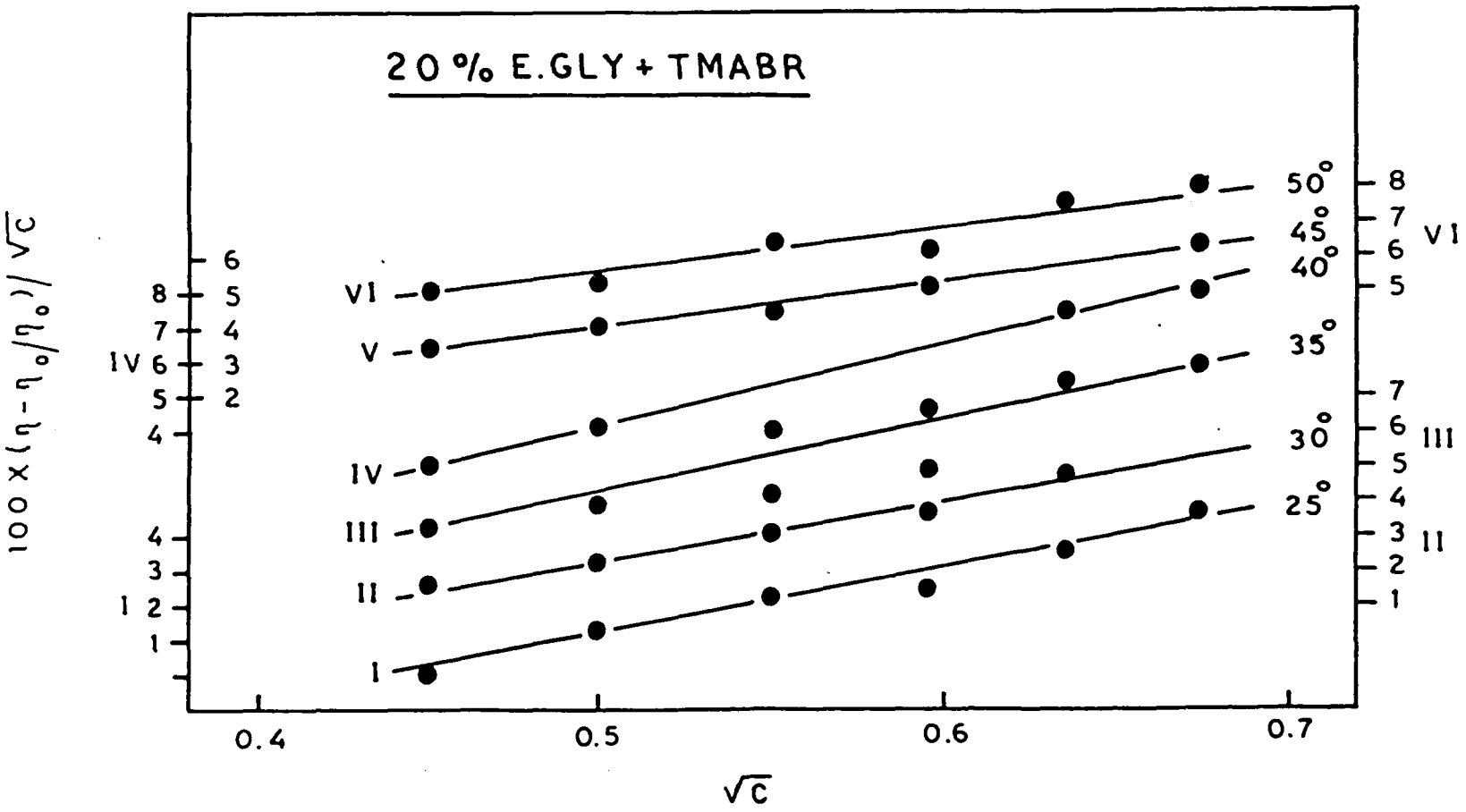

FIG.3.2. PLOTS OF $(\eta/\eta_o - 1)/\sqrt{C}$ Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL - WATER MIXTURE.

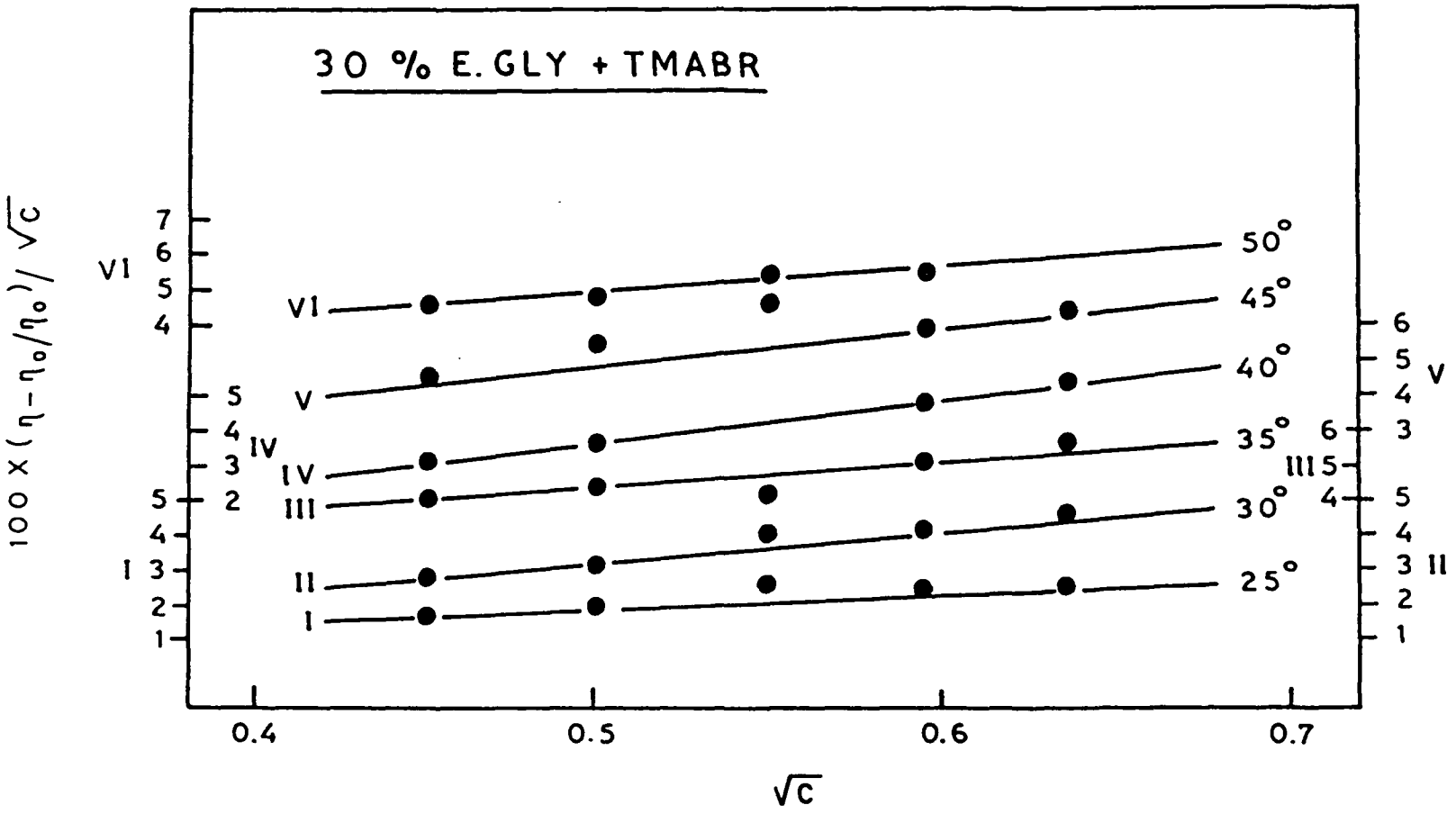

FIG. 3.3. PLOTS OF $(\eta/\eta_o - 1)/\sqrt{C}$ Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL - WATER MIXTURE.

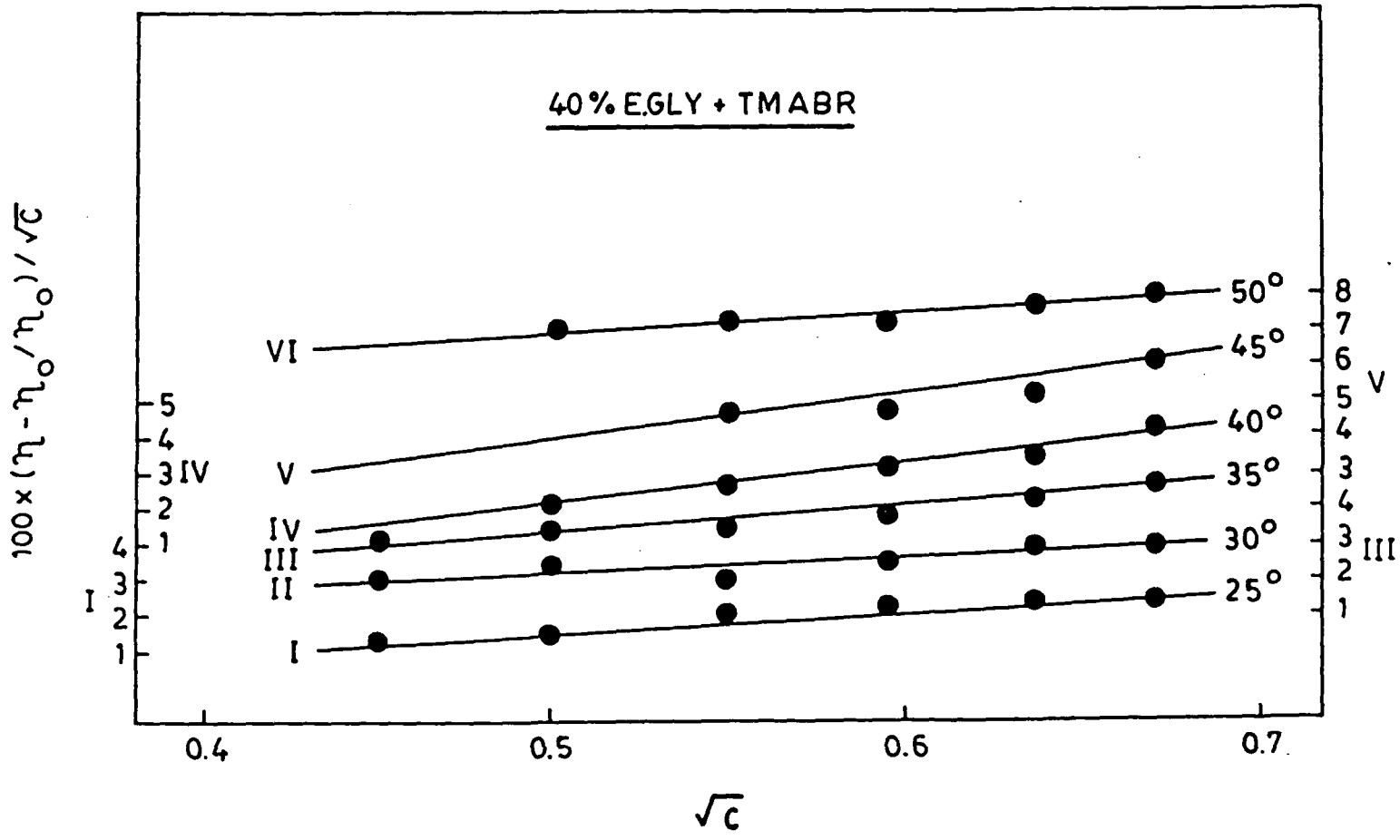

FIG. 3.4. PLOTS OF $(\eta/\eta_o - 1)/\sqrt{C}$ Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL-WATER MIXTURE.

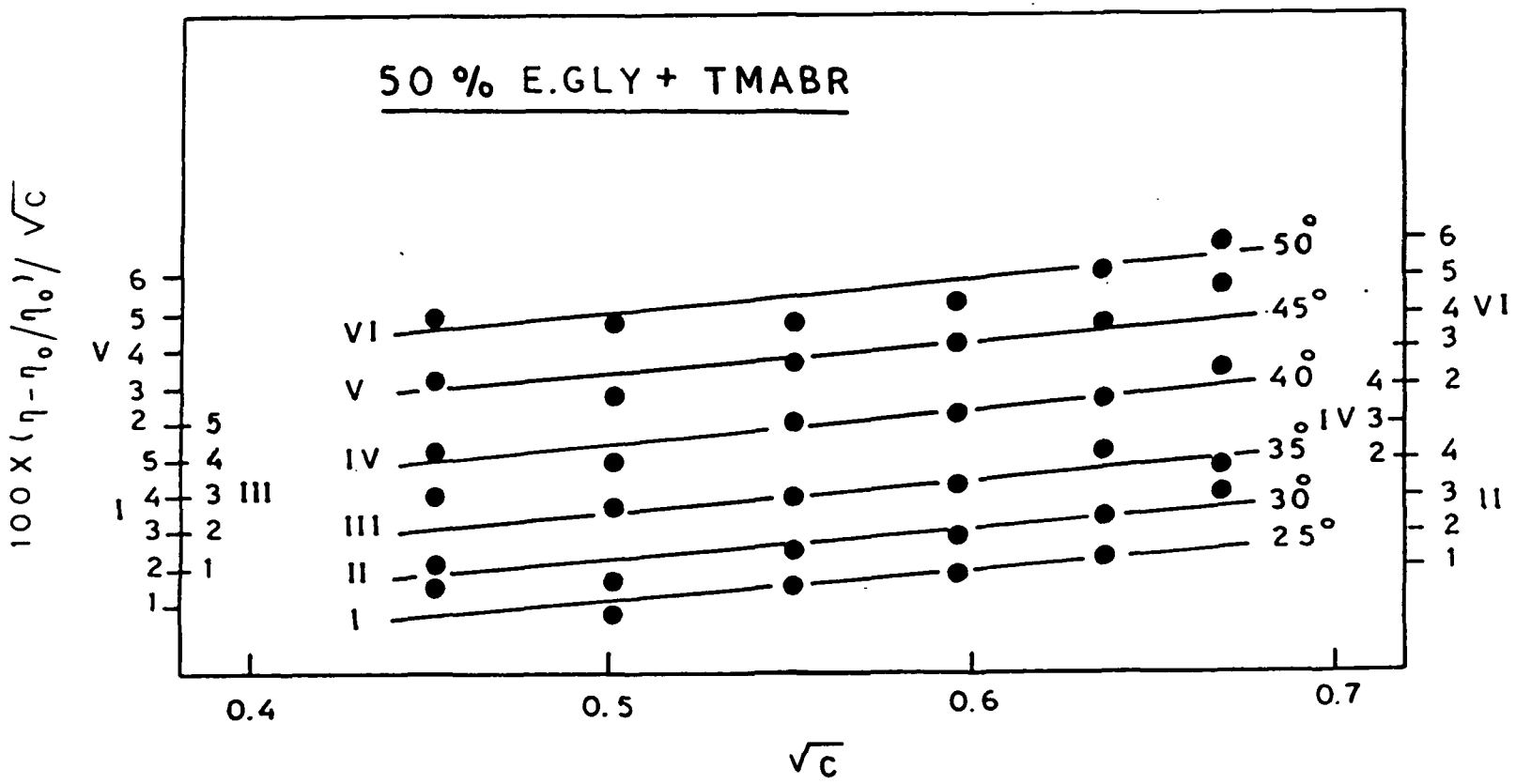

FIG.3.5. PLOTS OF $(\eta/\eta_o^{-1})/\sqrt{C}$ Vs. $\sqrt{C}$ FOR Me_4NBr IN ETHYLENE GLYCOL - WATER MIXTURE.

Table 4: Computed parameters of Eqn. (3) in 10, 20, 30, 40 and 50 W % Ethylene glycol–water mixture

Temperature	A	B	SD
	10 W % Ethylene glycol		
25	-0.074	0.15	0.0075
30	-0.069	0.15	0.0058
35	-0.089	0.19	0.0082
40	-0.066	0.16	0.0031
45	-0.022	0.11	0.0022
50	-0.0046	0.10	0.0033
	20 W % Ethylene glycol		
25	-0.075	0.18	0.0023
30	-0.070	0.19	0.0064
35	-0.065	0.20	0.0084
40	-0.044	0.17	0.0106
45	-0.032	0.14	0.0060
50	-0.012	0.13	0.0046
	30 W % Ethylene glycol		
25	-0.087	0.21	0.017
30	-0.109	0.28	0.014
35	-0.074	0.23	0.011
40	-0.043	0.15	0.028
45	-0.011	0.13	0.008
50	-0.074	0.24	0.012

Continued...

Table 4 continued

Temperature	A	B	SD
	40 W % Ethylene glycol		
25	-0.011	0.05	0.001
30	-0.010	0.07	0.002
35	0.0003	0.06	0.001
40	0.030	0.01	0.010
45	0.026	0.02	0.003
50	0.011	0.04	0.010
	50 W % Ethylene glycol		
25	-0.040	0.11	0.007
30	-0.050	0.12	0.005
35	-0.060	0.17	0.009
40	-0.03	0.11	0.002
45	-0.03	0.12	0.003
50	-0.002	0.08	0.004

It has also been found that the value of A decreases with increase in temperature due to more violent thermal agitation at higher temperature and therefore, the force of attraction diminishes. At relatively higher concentrations ($C \geq 0.15$) the values of A for most of the electrolytic solutions of tetra-methyl-ammonium bromide in ethylene glycol-water mixtures have been found negative and are without any significance. These results verify the findings of Dalian[152].

In 40 % ethylene glycol solution, the value of A-coefficient was positive, suggesting strong ion-ion interactions. This may be possible due to unusual cation-cation and cation-anion interactions as suggested by other workers[153, 154].

The positive B values in the case of tetra-methyl ammonium bromide indicate strong interactions of solvent molecules with the small bromide ions, which increase the formation of structures of the solvent molecules in its immediate vicinity. This indicates that the high charge density on the small cations (Me_4N^+) give rise to strong electrostatic ion-solvent interactions in solution. Hence the smaller the ion, the stronger is the ion-solvent dipole interaction and larger the size of the solvated ions in solution.

REFERENCES

REFERENCE

1. Breaslaw, B.R. and Millar, I.F., J. Phys. Chem., 74, 1056, (1970).
2. Eagland, D. and Pilling, G., J. Phys. Chem., 76, 1902, (1972).
3. (a) Gopal, R. and Singh, P., Ind. J. Chem., 14A, 388, (1976). (b) Islam, M.R. and Ansari, A.A., Ind. J. Chem., 21A, 1057, (1982).
4. Smid, J. and Grotens, A.M., J. Phys. Chem., 79, 2377, (1975).
5. Jones, G. and Dole, M., J. Am. Chem. Soc., 51, 2950, (1929).
6. Nightingale, E.R. (Jr.), J. Phys. Chem., 66, 894, (1962).
7. Miller, M.L. and Doran, M., J. Phys. Chem., 60, 186, (1959).
8. Falkenhagen, H., Z. Phys. Chem., 86, 159, (1929)
9. Gurney, R.W., "Ionic Process in Solution", McGraw Hill, New York, Chapter 9, (1953).
10. Janz, G. J., Oliver, B.G., Laksminarayanana, G.R. and Mayer, G.E., J. Phys. Chem., 74, 1285, (1970).
11. Kay, R.L. and Evans, D.F., J. Phys. Chem., 70, 3661, (1966), ibid, 70, 2325, (1966).
12. Treiner, C. and Fuoss, R.M., Z. Phys. Chem., 228, 343, (1965).
13. Evans, D.F., Zawoyski, C. and Kay, R.L., J. Phys. Chem., 69, 3878, 4216 (1965).
14. Kay, R.L., Zawoyski, C. and Evans, D.F., J. Phys. Chem., 69, 4208, (1965).

15. Kay, R.L., Evans, D.F. and Cunningham, P., J. Phys. Chem., 73, 3322, (1969).
16. Evans, D.F. and Gardam, P., J. Phys. Chem., 73, 158, (1969).
17. Evans, D.F. and Gardam, P., J. Phys. Chem., 72, 3281, (1968).
18. Serieno, R.F., Greco, P.W. Mamajeck, R.C., J. Phys. Chem., 75, 1722, (1971).
19. Evans, D.F., Thomas, J., Nadas, J.A. and Matesich, M.A., J. Phys. Chem., 75, 1714, (1971).
20. Evans, D.F. and Nadas, J. A., J. Phys. Chem., 75, 1708, (1971).
21. Mattina, C.F. and Fuoss, R.M., J. Phys. Chem., 79, 1604, (1975).
22. Fuoss, R.M., J. Phys. Chem., 79, 525, (1975).
23. Barker, B.J. and Caruso, J. Phys. Chem., 77, 1884, (1973).
24. Debye, P. and Huckel, E., Z. Physik, 24, 185, 305, (1923).
25. Onsager, L. Z. Physik, 26, 388, (1926).
26. Onsager, L., Trans. Faraday Soc., 23, 341, (1927).
27. Onsager, L. Z. Physik, 28, 277, (1927).
28. Shedlovsky, T., J. Am. Chem. Soc., 54, 1405, (1932).
29. Onsager, L. and Fuoss, R.M., J. Phys. Chem., 36, 2689, (1932).
30. Fuoss, R.M. and Hsia, K.L., Proc. Natl. Acad. Sci., U.S.A., 57, 1550, (1967).
31. Fuoss, R.M. and Onsager, L., Proc. Natl. Acad. Sci., U.S.A., 41, 274, (1955).
32. Fuoss, R.M. and Onsager, L., J. Phys. Chem., 61, 668, (1957).
33. Pitts, E., Proc. Roy. Soc. (A), 43, 217, (1953).

34. Fuoss, R.M., J. Am. Chem. Soc., 79, 3301, (1957).

35. Fuoss, R.M. and Kraus, C.A., J. Am. Chem. Soc., 79, 3304, (1957).

36. Lind, J.E. Jr. and Fuoss, R.M., J. Phys. Chem., 65, 999, (1961).

37. Falkenhagen, H., Z. Physik, 32, 745, (1931).

38. Falkenhagen, H. and Dole, M., Z. Phys. Chem., 30, 611, (1929).

39. Fuoss, R.M., J. Am. Chem. Soc., 80, 3163, (1958).

40. Fuoss, R.M., J. Am. Chem. Soc., 81, 2659, (1959).

41. Matesich, M.A., Nadas, J.A. and Evans, D.F., J. Phys. Chem., 74, 4568, (1978).

42. Renard, E. and Justice, J.C., J. Soln. Chem., 3, 633, (1974).

43. Justice, M.C., Buryed, R. and Justice, J.C., Electrochem. Acta, 16, 687, (1971).

44. Justice, J.C. and Fuoss, R.M., J. Phys. Chem., 67, 1707, (1963).

45. D'Aparno, A., Komiyama, J. and Fuoss, R.M., J. Soln. Chem., 4, 279, (1975).

46. D'Aparno, A. and Fuoss, R.M., J. Soln. Chem., 3, 45, (1974).

47. James, C.J. and Fuoss, R.M., J. Soln. Chem., 4, 91, (1975).

48. Fuoss, R.M., Proc. Natl. Acad. Sc., 75, 16, (1978).

49. Fuoss, R.M., J. Phys. Chem., 82, 2427, (1978).

50. Fuoss, R.M., "PARACOND", Dept. of Chemistry, Yale University, New Heaven, Connecticut, (1978).

51. Kay, R.L. and Evans, D.F., J. Phys. Chem., 69, 4216, (1965).

52. Kay, R.L., Hales, B.J. and Conningham, G.P., J. Phys. Chem., 71, 3925, (1967).

53. Kay, R.L., J. Am. Chem. Soc., 82, 2099, (1960).

54. Kay, R.L., Zawoyski, C. and Evans, D.F., J. Phys. Chem., 69, 4208, (1965).

55. Kay, R.L., Vituccio, T., Zawosyki, C. and Evans, D.F., J. Phys. Chem., 70, 2336, (1966).

56. Thomson, W.E. and Kraus, C.A., J. Am. Chem. Soc., 69, 1016, (1947).

57. Fuoss, R.M. and Hsia, K.L., proc. Natl. Acad. Sci., U.S.A., 57, 1550, (1967).

58. Fuoss, R.M., J. Am. Chem. Soc., 81, 2659, (1959).

59. Fuoss, R.M., J. Phys. Chem., 80, 2091, (1976).

60. Fuoss, R.M., Proc. Natl. Acad. Sci., U.S.A., 71, 4491, (1974).

61. Mattins, C.F. and Fuoss, R.M., J. Phys. Chem., 82, 2427, (1975).

62. Reichstadter, L., Fischerova, E. and Fischer, O., J. Soln. Chem., 22, 809, (1993).

63. Niazi, M.S.K., Fischer, O. and Fischerova, E., J. Soln. Chem., 15, 957, (1987).

64. Niazi, M.S.K., Bull. Chem. Soc. Jpn., 61, 2165, (1988).

65. Sanchez, M.M., Moran, C., Quintana, C. and Vivo, A., J. Soln Chem., 18, 993, (1989)

66. Nandi, D, Roy, M.N. and Hazra, D.K., J. Indian Chem. Soc., 70, 305, (1993).

67. D'Aprano, A., Capalbi, A. and Battistini, M., J. Electronal. Chem., 353, 121, (1993).

68. Sayal, V.K. and Bisht, P., Indian J. of Chem. Tech., 1, 233, (1994).

69. Srivastva, A.K. and Shivdas, R., J. Electronal. Chem., 399, 235, (1995).

70. Dash, U.N. and Patnaik, E.R., Indian J. Chem., 34A, 556, (1995).

71. Dash, U.N. and Mohanty, B.K., Indian J. Chem., 35A, 983, (1996).

72. D'Aprano, A., Sesta, B., Capalbi, A., Iammarino, M. and Mauro, V., J. Electronal. Chem., 403, 257, (1996).

73. Bhat, J.I. and Gaonkar, S.G., J. Indian Chem. Soc., 75, 304, (1998).

74. Vogal, I., "A textbook of practical organic Chemistry", Longmans, Green and Co. London, New York, Toronto, pp.103-106, (1924).

75. Mattina, C.F. and Fuoss, R.M., J. Phys. Chem., 79, 1604, (1965).

76. Eiji Kubota and Masatoki Yokoi, Bull. Chem. Soc. Japan, 50(6), 1425, (1977).

77. Cannon, M.R., Manning, R.W. and Bell, J.D., Anal. Chem., 32, 355, (1960).

78. Harned, H.S. and Owen, B.B., "The Physical Chemistry of Electrolytic Solutions", Reinhold Pub. Corp., New York, p.161, (1958).

79. "International Critical Tables of Numerical data Physics, Chemistry and Technology", McGraw Hill Book Co., New York, (a) Vol. III, p. 27, (1930), (b) Vol. VII, p. 220 (1930).

80. Lind, J.E., Zwolenik, J.J. and Fuoss, R.M., J. Am. Chem. Soc., 81, 1557, (1959).

81. Kay, R.L., Zawoyski, C. and Evans, D.F., J. Phys. Chem., 69, 4208, (1965).

82. Barker, B.J. and Caruso, J.A., J. Phys. Chem., 77, 1884, (1973).

83. Fuoss, R.M., Onsager, L. and Skinner, J.F., J. Phys. Chem., 69, 2581 (1965).

84. Justice, J.C., J. Chem. Phys., 65, 353, (1968).

85. Pitts, E., Tabor, B.E. and Daly, J., Trans. Faraday Soc., 65, 894, (1969).

86. Fuoss, R.M., J. Phys. Chem., 71, 1829, (1977).

87. Saloman, M. and Plichta, E., Electrochemica Acta, 28, 1681, (1983).

88. Fuoss, R.M. Aceascina, F., Electrolytic Conductance Interscience, New York, (1959).

89. Kay, R.L., J. Am. Chem. Soc., 82, 2099, (1960).

90. Islam, M.R. and Ansari, A.A., Indian J. Chem., 26A, (1988).

91. Ansari, A.A. and Islam, M.R., 66, 1223, (1988).

92. Ansari, A.A. and Islam, M.R., 66, (1988).

93. Thomas, J. and Evans, D.F., J. Phys. Chem., 74, 3812, (1970).

94. Coetzee, J.F. and Cunningham, G.P., J. Am. Chem. Soc., 87, 2529, (1965).

95. Mateshich, S.M.A., Nadas, J.A. and Evans, D.F., J. Phys. Chem., 74, 4568, (1970).

96. Broadwater, T.L. and Evans, D.F., J. Phys. Chem., 73, 3985, (1969).

97. Lee, W.H. and Wheaton, R.J., J. Chem. Soc. Faraday Trans. II, 75, 1128, (1979).

98. Beronius, P. Acta Chem. Scand, A. 34, 309, (1980).

99. Bahadur, L. and Ramanamurti, M.V., J. Chem. Soc. Faraday I, 76, 1409, (1980).

100. (a) Irani, E.P. J. Am. Chem. Soc., 65, 1396, (1944).
(b) Kenttamma, J., Tommila, E. and Marlti, M., Ann-Acad. Sci. Fenn., Ser. A.2, 1, (1959).

101. Kay, R.L. and Broadwater, T.L., J. Soln. Chem. 5, 57, (1976).

102. Kay, R.L. and Broadwater, T.L., Electrochemica Acta, 16, 667, (1971).

103. D'Aprano, A. and Fuoss, R.M., J. Phys. Chem., 67, 1704, (1963).

104. Stokes, R.H. and Mills, RF., "Viscosity of Electrolytes and Related Properties", Pergamon Press, Inc., New York, 1965, p. 54.

105. Broadwater, T.L. and Kay, R.L., J. Phys. Chem., 74, 3802, (1970).

106. Bahadur, L. and Ramanamurti, M.V., Can. J. Chem., 62, 1051, (1984).

107. Vissar, C. de and Samson, G., J. Phys. Chem., 78, 1719, (1974).

108. Visser, C. de and Samson, G., J. Soln. Chem., 3, 847, (1974).

109. Desnoyers, J.E. and Perron, G., J. Soln. Chem., 1, 199, (1972).

110. Justice, J.C., J. Phys. Chem., 79, 454, (1975).

111. Sears, P.G., Wilhoit, D. and Danson, L.R., J. Phys. Chem., 59, 373, (1955).

112. Hughes, S.R.C. and Price, D.H., J. Chem. Soc., A., 7, 1093, (1967).

113. Rasaiah, J.C., J. Chem. Phys., 52, 704, (1970).

114. William, R. Gilkerson and Katherine, L., Kendrick, J. Phys. Chem., 88, 5352, (1984).

115. Bjerrum, N.K. Mat, -Fys. Medd-K. Dan-Vidensk. Selsk. 7, No. 9, (1926).

116. Goffredi, M. and Shedlovsky, T., J. Chem. Phys., 71, 2176, ibid, 2182, (1967).

117. Ramanamurti, M.V., Prabhu, P.V.S.S. and Bahadur, S.L., Bull. Chem. Soc. Jpn., 59, 2341, (1986).

118. Das, M.N. and Kundu, K.K., J. Indian Chem. Soc., 51, 266, (1974).

119. Kundu, K.K. and Das, A.K., Ind. J. Chem., 16(A), 467, (1978).

120. Kundu, K.K., Chattopadhyay, P.K., Jana, D. and Das, M.N., J. Phys. Chem., 74, 2633, (1970).

121. Zipp, A.P., J. Chem. Phys., 77, 718, (1973).

122. Masterton, W.L. and Biery, T., J. Phys. Chem., 74, 139, (1970).

123. D'Aprano and Fuoss, R.M., J. Am. Chem. Soc., 91, 279, (1969).

124. Singh, N.P. and Prasad, B.N., Indian J. Chem., 14A, 659, (1976).

125. Gopal, R., Kumar, R. and Agarwal, D.K., Indian J. Chem., 14A, 803, (1976).

126. Gibson, R.E. and Kincard, J.F., J. Am. Chem. Soc., 59, 579, (1937).

127. Hamann, S.D. and Lim, S.C., Aust. J. Chem., 7, 329, (1954).

128. Gopal, R.M. and Shrivastava, R.K., J. Phys. Chem., 66, 2704, (1962), J. Ind. Chem. Soc. 40, 99, (1963).

129. Millero, F.J., J. Phys. Chem., 72, 3209, (1968).

130. Kawaizumi, F. and Zana, R., J. Phys. Chem., 78, 627, (1974), ibid, 78, 1099, (1974).

131. Millero, F.J., Chem. Rev., 71, 147, (1971).

132. Redlich, O. and Meyer, D.M., Chem. Rev., 64, 221, (1964).

133. Bateman, R.L., J. Am. Chem. Soc., 71, 2291, (1949), ibid, 74, 5516, (1952).

134. Padova, J., J. Chem. Phys., 39, 2599, (1963).

135. Devi, S. and Das, P.B., J. Ind. Chem. Soc., 42, 501, (1965).

136. Das, N.C., Mohapatra, H. and Das, P.B., J. Ind. Chem. Soc., 43, 373, (1966).

137. Lee, I. and Hyne, J.B., Can. J. Chem., 46, 2333, (1968).

138. Macdonald, D.D. and Hyne, J.B., Can. J. Chem., 48, 2416, (1970).

139. Masson, D.O., Phil. Mag., (7), 8, 218, (1929).

140. Falkenhagen, H. and Vernon, E.L., Philos. Mag., 14, 537, (1932).

141. Cox, W.M. and Wolfenden, J.H., Proc. Roy. Soc. Ser., A 145, 425, (1934).

142. Kaminskay, M., Discuss. Faraday Soc., 24, 171, (1957).

143. Robinson, R.A. and Stokes, R.H., Electrolytic Solutions, 2nd. Ed., Butter-Worth, London, (1959).

144. Asmus, V.E. and Naturforsch, Z., 49, 589, (1949).

145. Glasstone, S., Laidler, K.J. and Eyring, H., The Theory of Rate Processes, McGraw Hill Book Co., Inc. New York, N.Y., (1941).

146. Pandey, J.D. and Akhtar, Y, Indian J. Chem., 36A, 614, (1997).

147. Nikam, P.S., Ansari, H.R. and Hasan, M., J. Indian Chem. Soc., 76, 344, (1999).

148. Mandal, K.K. and Haldar, P., J. Indian Chem. Soc., 77, 201, (2000).

149. Lamb, A.B. and Lee, R.E., J. Am. Chem. Soc., 35, 1666,(1913).

150. Geffcken and Price, D., Z. Physik, Chem., B26, 81, (1934).

151. Sen Utpal, J. Phys. Chem., 80, 1569, (1976).

152. Dalian, F.E. and Briscoe, H.T., J. Phys. Chem., 41, 1129, (1937).

153. Gopal, R. and Siddiqi M.A., Z. Phys. Chem., Neuetolge, 67, 122, (1969).

154. Gopal, R. and Singh, K., Z. Phys. Chem., Neuetolge, 68, 81, (1970).